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**THE**  
**STUDENT'S HAND-BOOK**  
**OF**  
**CHEMISTRY**





THE  
STUDENT'S HAND-BOOK  
OF  
CHEMISTRY

WITH  
TABLES AND CHEMICAL CALCULATIONS

BY  
H. LEICESTER GREVILLE, F.I.C., F.C.S.

*Chemist to the Commercial Gas Company, London  
For many years Chief Assistant in the Chemical Laboratory, Metropolitan  
Board of Works*



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## PREFACE

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IN the presence of so many good manuals on Chemistry, the appearance of another may seem unnecessary, yet the writer may be permitted to hope that his book will be of use to the student, for whom it is intended. An attempt has been made to simplify the subject as much as possible ; and also to supply a want felt by most students with regard to general chemical calculations. Examples of these have been given where thought necessary, and the principles on which they are based explained. By the use of tables much information has been compressed into a small space, and given in a form that it is hoped will render it readily accessible to the student.



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**PART I.**



# THE STUDENT'S HAND-BOOK

OF

## CHEMISTRY

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### CHAPTER I

#### DEFINITION OF CHEMICAL SCIENCE—DISTINCTION BETWEEN MECHANICAL MIXTURE AND CHEMICAL UNION—ELEMENTS AND COMPOUNDS.

**T**HE SCIENCE OF CHEMISTRY has for its object the investigation of the composition and character of the various substances, solid, liquid, and gaseous, which are found in Nature, and of the laws which regulate their combination and decomposition. A *chemical* action is said to take place when substances, either by action on each other, or by subjection to particular conditions, are so changed that new bodies are formed, differing entirely from the originals in their character and properties. If, for instance, we take iron filings and sulphur, and mix them together, however intimately, we never obtain anything but a simple mechanical mixture, in which, under the microscope, the separate particles of iron and sulphur are distinctly visible. From such a mixture, made mechanically, we can recover the constituent elements equally mechanically; *for the iron filings may be entirely separated by the use of a magnet, leaving the sulphur behind in its*

original form. Let us, however, apply heat to the mixture, and a *chemical* union at once takes place between the two substances—a black, heavy, brittle mass being obtained, differing most essentially from either of its constituents, both in its physical and chemical characteristics. By suitable means the whole of the sulphur on the one hand, and the iron on the other, may be recovered in their original forms; but their presence cannot be identified by simply mechanical means—chemical action has caused their union, and chemical action alone can occasion their separation. Again, let us take some of the substance produced in the last experiment—a compound known as sulphide of iron, or ferrous sulphide—and pour upon it some dilute sulphuric acid; a brisk effervescence ensues, from the escape of a gas formed by the union of the original sulphur with hydrogen, the ferrous sulphide gradually disappears, and there finally remains a green solution containing iron in combination with sulphuric acid as a compound, called sulphate of iron. Here chemical union and chemical decomposition have both taken place; for the sulphuric acid has decomposed the ferrous sulphide, united with the iron, while the sulphur has passed off in union with hydrogen as an invisible gas. From the action of one compound (sulphuric acid) on another compound (ferrous sulphide), two entirely different compounds have been formed—viz., sulphate of iron and sulphuretted hydrogen. When any combustible material is burnt in the air, it is noticed to slowly disappear, and is apparently lost. Such, however, is not the case. Here, again, chemical action is taking place. In the case of a candle, for instance, its combustion is in reality a combination of the constituents carbon and hydrogen with the oxygen of the air. No loss of matter occurs; for if the products of combustion are collected, which can easily be *performed by suitable means*, the total weight of such *products is found to be equal to the weight of the*

candle which has been consumed, *plus* the oxygen of the air with which it has united.

Chemistry is essentially an *experimental science*. Its growth as a science dates from the invention of mechanical appliances which allowed the performance of exact experiments. Before the construction of delicate balances and apparatus, by which quantitative experiments could be performed with exactness, the elaboration of the present system of chemical philosophy, which enables chemistry to be an exact science, was almost impossible. All the principal substances found in Nature have now been examined by the chemist, and their individual properties and actions on each other under varying conditions ascertained; and by such examination it has been found that one broad classification could be instituted between entirely different groups of substances. The substances of one class have resisted all attempts which have been made to resolve them into simpler forms, and such materials are termed "elements." The other class is formed by the chemical union of these elements with each other in definite proportions, and the results are termed *compounds*. The chief materials found on the surface of the earth are compounds, comparatively few substances being met with naturally in the elementary condition. Chalk, water, sugar, and salt may be taken as familiar examples of compound bodies, for they can all be resolved into simpler forms. Chalk, for instance, is composed of the metal calcium united with oxygen and carbon; water is composed of oxygen and hydrogen; sugar, of carbon, oxygen, and hydrogen; and salt, from the union of chlorine with the metal sodium. Neither calcium, oxygen, hydrogen, carbon, chlorine, or sodium can, however, be resolved into simpler forms, and they are consequently termed elements, or elementary bodies. Of these elements there are sixty-three in number *at present known*. Of these, two at the ordinary temperature of the air are liquids, viz., bromine

and mercury; four are gases—hydrogen, oxygen, nitrogen, and chlorine; and the rest are solids. The distinction, however, between the gaseous, the liquid, and the solid conditions of matter is simply physical, and dependent on temperature and pressure; for many of the elements can be made by alterations of temperature or pressure, or of both combined, to assume either the gaseous, the liquid, or the solid condition, as desired.

On examining the physical appearance and characteristics of the elements, besides the distinction between gaseous, liquid, and solid, a further distinction will be observable—viz., the possession by some considerable number of a peculiar brightness when polished, known as the “metallic lustre.” This property is generally combined with great weight and power of conducting electricity and heat. Elements which possess the above properties are known as metals, and the elementary bodies are for convenience arbitrarily divided into Metals and Non-Metals. In the whole number of elements there are forty-eight Metals and fifteen Non-Metals; one metal only is liquid, viz., mercury, the rest being solid. Of the fifteen non-metals, one is liquid (bromine), four are gaseous, and the remainder are solids.

A complete list of the elementary bodies is here given, in which the plan has been adopted of printing the non-metallic bodies in large type (IODINE), the commoner metals in small capitals, and the rarer and less-occurring metals in italics:—

<i>Names</i>	<i>Symbols</i>	<i>Atomic Weights</i>
ALUMINIUM . . . . .	Al	27·4
ANTIMONY (Stibium) . . . . .	Sb	122
ARSENIC . . . . .	As	75
BARIUM . . . . .	Ba	137
<i>Beryllium, or Glucinum</i> . . . . .	Be	9·3
BISMUTH . . . . .	Bi	210
BORON . . . . .	B	11
<b>BROMINE</b> . . . . .	Br	80
<i>Cadmium</i> . . . . .	Cd	112

<i>Names</i>	<i>Symbols</i>	<i>Atomic Weights</i>
<i>Caesium</i> . . . . .	Cs	133
CALCIUM . . . . .	Ca	40
CARBON . . . . .	C	12
<i>Cerium</i> . . . . .	Ce	92
CHLORINE . . . . .	Cl	35·5
CHROMIUM . . . . .	Cr	52·2
COBALT . . . . .	Co	58·7
COPPER (Cuprum) . . . . .	Cu	63·5
<i>Didymium</i> . . . . .	D	95
<i>Erbium</i> . . . . .	E	112·6
FLUORINE . . . . .	F	19
GOLD (Aurum) . . . . .	Au	197
HYDROGEN . . . . .	H	1
<i>Indium</i> . . . . .	In	113
IODINE . . . . .	I	127
<i>Iridium</i> . . . . .	Ir	198
IRON (Ferrum) . . . . .	Fe	56
<i>Lanthanum</i> . . . . .	La	92
LEAD (Plumbum) . . . . .	Pb	207
<i>Lithium</i> . . . . .	Li	7
MAGNESIUM . . . . .	Mg	24
MANGANESE . . . . .	Mn	55
MERCURY (Hydrargyrum) . . . . .	Hg	200
<i>Molybdenum</i> . . . . .	Mo	96
NICKEL . . . . .	Ni	58·7
<i>Niobium</i> . . . . .	Nb	94
NITROGEN . . . . .	N	14
<i>Osmium</i> . . . . .	Os	199·2
OXYGEN . . . . .	O	16
<i>Palladium</i> . . . . .	Pd	106·6
PHOSPHORUS . . . . .	P	31
PLATINUM . . . . .	Pt	197·5
POTASSIUM (Kalium) . . . . .	K	39·1
<i>Rhodium</i> . . . . .	Rh	104·4
<i>Rubidium</i> . . . . .	Rb	85·4
<i>Ruthenium</i> . . . . .	Ru	104·4
SELENIUM . . . . .	Se	79·5
SILVER (Argentum) . . . . .	Ag	108
SILICON . . . . .	Si	28
SODIUM (Natrium) . . . . .	Na	23
STRONTIUM . . . . .	Sr	87·5
SULPHUR . . . . .	S	32
<i>Tantalum</i> . . . . .	Ta	182
TELLURIUM . . . . .	Te	129
<i>Thallium</i> . . . . .	Tl	204



<i>Names</i>	<i>Symbols</i>	<i>Atomic Weights</i>
<i>Thorium</i> . . . . .	Th	231·5
<i>TIN</i> (Stannum) . . . . .	Sn	118
<i>Titanium</i> . . . . .	Ti	50
<i>Tungsten</i> . . . . .	W	184
<i>Uranium</i> . . . . .	U	240
<i>Vanadium</i> . . . . .	V	51·3
<i>Yttrium</i> . . . . .	Y	61·6
<i>ZINC</i> . . . . .	Zn	65·2
<i>Zirconium</i> . . . . .	Zr	89·6

These elements, from their mutual combination, form the numerous substances found in and about the earth. Their distribution is very varied, and their respective quantities exceedingly different, for while some are only met with in such minute quantities as to make thorough investigation extremely difficult, others are met with so plentifully and universally as to be almost omnipresent. For example, caesium, didymium, erbium, and indium are met with in exceedingly small quantities, whereas such elements as oxygen, hydrogen, silicon, aluminium, calcium, and carbon are all more or less plentiful. In seas, lakes, and rivers we have an almost unlimited store of oxygen and hydrogen in the form of water; oxygen occurs in the free state in the atmosphere mixed with nitrogen; silicon occurs in union with oxygen, as flint, quartz, and rock crystal, and as the basis of sands and sand-stones; aluminium occurs in union with silica, as clay; calcium in union with carbonic acid, as chalk, marble, and limestone; while carbon is found in the atmosphere as carbonic acid, and forms the basis of the various descriptions of coals and lignites, as well as of the whole structure of animal and vegetable life.

That the number of really existing elements is limited to those now known, is doubtful, if not improbable. It is at least possible that others will be discovered in the future, with the continually increasing *appliances and fresh methods of investigation*. Several *new elements* previously unrecognised were brought to *light on the introduction of spectrum analysis alone*.

and it is therefore impossible to limit the existing elementary bodies to those now known. Further research may also, on the other hand, diminish the number of elements; for an increased command over the forces of nature may enable the chemist to prove that many elementary substances now regarded as distinct from each other, are in reality but modifications of the same form of matter.

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## CHAPTER II.

### GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY—LAWS OF EQUIVALENCY AND OF MULTIPLE PROPORTION—DALTON'S ATOMIC THEORY.

In the previous chapter it has been shown that one broad distinction could be made between the various substances found in nature, into compounds and elements, a list of the latter being given. In the investigation into the composition of the various forms of matter, it has not only been proved that the elements are capable of uniting with one another to form compounds differing entirely in character from the original materials, but it has also been shown that such combinations always take place in definite proportions. Thus, not only does chlorine unite with sodium to form sodium chloride, or common salt, but such combination invariably takes place in the proportion of 35.5 of chlorine to 23 of sodium. Again, in the union of sulphur with iron to form the compound known as "Ferrous sulphide," to which attention has already been directed, the combination of the two substances always occurs in the proportion of 32 parts of sulphur to 56 of iron. Not only is this the case, but the *proportions representing the combination of sodium with chlorine, and of iron with sulphur, also represent*

the proportions in which sulphur can unite with sodium, or chlorine with iron. Each of the elements has thus a number attached to it, which represents the proportion in which it combines with any of the others, and these numbers are called equivalent or combining weights, and the law which expresses this numerical relation of combination is termed *the law of combining proportion*. The combining weights represent, as a rule, the *smallest* proportionate number (avoiding fractions) in which the elements can unite with each other. Simple compounds are not only formed by the union of single combining proportions of the elements with each other, but several combining proportions of one or another element may be present in a compound; thus oxygen unites with hydrogen to form two distinct compounds,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ , the one of which contains two combining proportions of hydrogen to one of oxygen, and the other equal equivalents of each element.

Again, oxygen unites with nitrogen to form five distinct compounds in which the proportions of the two elements are as follow:—

1	Nitrogen	28	(14 × 2)	Oxygen	16
2	"	28	"	"	32 (16 × 2)
3	"	28	"	"	48 (16 × 3)
4	"	28	"	"	64 (16 × 4)
5	"	28	"	"	80 (16 × 5)

Other examples could be given, but as they will be met with continually throughout the work it is needless to multiply instances. The capability of the elements of uniting the one with the other in varying multiples of the respective combining weights is termed *the law of Multiple Proportion*.

Thus far it has been shown that combination ensues among the elements in the proportion of fixed quantities, and that the numbers representing these amounts are termed "*combining or equivalent weights*;" also that *chemical union* always ensues in these proportions or

some simple multiples of them. In compounds of oxygen, for instance, we must have, entering into combination, either 16 or some multiple of 16, such as 32, 48, etc.; with chlorine we must have either 35.5 parts or some multiple, such as 71, 106.5, etc. Never, in any case, can any intermediate quantity take part in a chemical union, and that which is correct for oxygen and chlorine, the two examples given, is equally correct in the case of all the other elements without exception. In order to afford some explanation of this peculiar property of the elements, Dr Dalton, who was likewise the first to enunciate the law of multiple proportion, proposed his now celebrated "Atomic Theory." By this theory it is assumed that all matter consists of *chemically* indivisible particles which are called "atoms," and which are of different weights in the various elements. The *absolute* weight of the atoms is not known, but their *relative* weights are assumed to be in the same proportion as that of the respective combining proportions of the corresponding elements; thus, assuming the weight of the hydrogen atom as 1, that of oxygen 16, that of chlorine 35.5, that of iron 56, and so on.

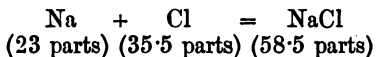
It is also assumed that chemical combination takes place by the juxtaposition or approximation of the atoms: thus, water is formed from one atom of oxygen weighing 16, and two atoms of hydrogen weighing 2 ( $16 + 2$ ); ferrous sulphide is produced from the chemical union of single atoms of iron and sulphur, weighing 56 and 32 respectively. Common salt consists of one atom of sodium weighing 23, and one of chlorine weighing 35.5. It will thus be seen that the atomic theory affords an explanation of the fact of chemical combination occurring in fixed quantities, and enables us to understand the reason that intermediate quantities of the elements are not found to take part in chemical reactions. The student must, however, bear in mind that the atomic theory is only a convenient mode of explaining the known facts upon

which the laws of elemental equivalency and of multiple proportion are dependent. A slight extension of the original views of Dr Dalton has been lately adopted, with the object of extending the applications of the atomic theory to a wider field. The study of particular chemical reactions has led the chemist to assume that it is at least probable that single atoms never take part in the formation of compounds, or in the mutual reaction of such compounds, but that *groups of atoms* are always involved. These groups are termed "molecules," a term also applied to the smallest portion of any chemical compound which can be conceived to exist in the free state. A molecule is supposed to be indivisible by mechanical means, the constituent atoms only suffering separation on the application of chemical means. It is important that a clear understanding should be formed of the respective terms "atom" and "molecule," as they are both of frequent occurrence in chemical language. We may therefore give a concise definition of each. An *atom* is the smallest part of an element which can exist in a chemical compound. A *molecule* is the smallest part of an element or compound which can exist in the free state, or which can take part in any chemical reaction.

#### CHEMICAL EQUATIONS

In the list of elements given in the first chapter a symbol was attached to each element, being either the initial letter of its English or Latin name, or the first two letters of either. Thus, hydrogen is represented by the initial letter or symbol H, oxygen by O, nitrogen by N, while for iron we have Fe (from its Latin name Ferrum), potassium K (from Kalium), and copper Cu (from Cuprum). Each of the elementary bodies is thus represented by its corresponding symbol, these *abbreviated expressions* constitute the chemist's *shorthand alphabet*, and enable him to express concisely in

writing facts which would otherwise occupy considerably more space to describe. These symbols have a double meaning attached to them, for not only are they abbreviated expressions of the names of the elementary bodies, but they have also a quantitative meaning in addition: thus, O not only stands for oxygen, but also for 16 parts of that element, while H represents 1 part of hydrogen, N 14 parts of nitrogen, Cl 35.5 parts of chlorine, and so on for all the other elements. We have thus the means of concisely expressing chemical reactions in the form of *equations*, in which we place the substances entering into combination, or the compounds acting on each other, on the left hand, and the products formed on the right, with a sign of equality between, thus =. The sign + is used between substances or compounds acting on each other, and compounds are represented by the juxtaposition of the individual elements; thus the equation  $\text{Na} + \text{Cl} = \text{NaCl}$  shows the formation of common salt from sodium and chlorine. An equation, it must be remembered, not only indicates what elements are involved and what compounds formed, but it likewise expresses the exact quantities of each which take part in the reaction. Thus the equation given not only indicates that sodium and chlorine unite to form sodium chloride, but that the reaction takes place in equivalent proportions, thus:—



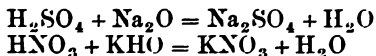
The test of the correctness of an equation, assuming of course that the reaction represented is chemically possible, is that the sum of the quantities on each side shall be equal. Thus, in the case given, 23 parts of sodium and 35.5 parts of chlorine give a total of 58.5 parts, and this is also the exact amount found on the other side of the equation. When more than one equivalent of any elementary body is present in a compound, the number of equivalents is represented by a small

figure appended to the right of the symbol; thus,  $\text{H}_2\text{SO}_4$  represents a compound of two equivalents of hydrogen, one of sulphur, and four of oxygen. Where more than an equivalent of a compound body takes part in a chemical action, the fact is usually represented by placing a large figure to the left of the compound; thus,  $2\text{H}_2\text{SO}_4$  represents two equivalents of  $\text{H}_2\text{SO}_4$  (sulphuric acid). Sometimes the same fact is represented by bracketing the compound and placing a small figure to the right; thus,  $(\text{NH}_3)_2$  represents two whole equivalents of  $\text{NH}_3$  (ammonia).

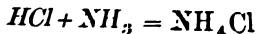
#### CHEMICAL NOMENCLATURE

Before proceeding to the actual description of the various elements, it will be advisable to give a short *resumé* of the principles which regulate the *naming* of chemical compounds, or, as it is more shortly termed, chemical nomenclature. With regard to the elements no general principles can be traced to underlie their nomenclature, which is almost entirely empirical and has a variety of derivations too numerous to come within the scope of the present work. With regard to compounds, however, their nomenclature was always more or less systematic, although considerable progress in a really scientific classification has been effected of late years, more especially in the domain of organic chemistry. The distinction between elements and compounds has already been sufficiently explained, and the meaning of these terms is therefore assumed to be understood. All substances formed from the union of elements are termed compounds, but the characteristics of these compounds are so varied that further distinctive terms are rendered desirable; and we have therefore in common use such terms as acids, bases, and salts, the latter of which may be again divided into *acid*, *neutral*, and *basic* compounds. An *acid compound*, or "*acid*," is generally characterised by a

more or less strongly marked sour taste, a capability of turning vegetable blues to red, and of uniting with bases to form salts. Sulphuric, hydrochloric, nitric, and oxalic acids may be taken as typical examples. There are two classes of acids, viz., the *hydracids*, which do not contain oxygen, such for instance as hydrochloric acid  $\text{HCl}$ , hydriodic acid  $\text{HI}$ , and the *oxyacids*, which contain oxygen, such as sulphuric acid  $\text{H}_2\text{SO}_4$ , and nitric acid  $\text{HNO}_3$ . Acids are spoken of as mono-basic, di-basic, tri-basic and tetra-basic, according to whether they contain one, two, three, or four atoms of hydrogen replaceable by a base to form a salt. Bases possess the reverse properties to acids, that is to say, they generally have an alkaline reaction, they restore the colour to reddened vegetable blues, and neutralise acids. Potash, soda, and ammonia, may be taken as good examples of alkaline bases. Bases may be divided into three classes, viz., metallic oxides, such as these of potash  $\text{K}_2\text{O}$ , soda  $\text{Na}_2\text{O}$ , calcium  $\text{CaO}$ , and iron  $\text{FeO}$ ; metallic hydrates, such as sodium and potassium hydrates  $\text{NaHO}$  and  $\text{KHO}$ , and calcic hydrate  $\text{CaH}_2\text{O}_2$ ; and compound bases such as ammonia  $\text{NH}_3$ . The term *salt* is generally used to designate the product of the union of an acid with a base, and is termed *acid* or *basic*, according to which constituent character predominates, or *neutral* in the event of both constituents being so proportioned to each other that the product is neither acid on the one hand nor alkaline on the other. In the formation of salts from the action of bases on metallic oxides and hydrates water is eliminated, thus:—



While in the formation of a salt by the union of such a base as ammonia with an acid, no elimination of water takes place, thus:—





The name of an acid is generally regulated by the name of what may be regarded as the distinctive element which it contains; thus, the compound of nitrogen, represented by the formula  $\text{HNO}_3$ , is termed "Nitric Acid," and that of sulphur, represented by the formula  $\text{H}_2\text{SO}_4$ , "Sulphuric Acid." Where an element forms more than one acid compound containing different proportions of oxygen, the compound containing the lesser quantity of oxygen is characterised by the termination "ous," while to that containing the greater quantity of oxygen, the termination "ic" is applied—thus we have sulphurous acid  $\text{H}_2\text{SO}_3$ , sulphuric acid,  $\text{H}_2\text{SO}_4$ , also nitrous acid  $\text{HNO}_2$ , and nitric acid  $\text{HNO}_3$ . The salts formed by the union of these acids with bases are characterised by the terminations "ite" and "ate"—thus, sulphurous acid gives "sodium sulphite," and sulphuric acid "sodium sulphate." In cases where a series of acids are known containing the same element united to several different proportions of oxygen, other prefixes are used. Thus chlorine forms four distinct acids, the two intermediate ones being known as chlorous and chloric acids, the one containing less oxygen than the chlorous is distinguished by the prefix "hypo," thus we have hypochlorous acid forming hypochlorites, while the one containing a greater quantity of oxygen than chloric is called *perchloric* acid.

The hydracids, that is, those compounds formed from the union of such elements as sulphur, chlorine, bromine, iodine, fluorine, with hydrogen, all terminate in "ic," and form salts ending in "ide;" thus we have hydro-sulphuric, hydro-chloric, hydro-bromic, hydriodic, and hydro-fluoric acids, forming respectively sulphides, chlorides, bromides, iodides, and fluorides.

Oxygen compounds are known as oxides; and as this substance in many cases unites in several proportions with the other elements, prefixes are used to indicate *the number of oxygen atoms present in the compounds*, thus *mon-oxides*, *di-oxides*, *tri-oxides*, *tetra-oxides*,

and pent-oxides, as the compounds contain one, two, three, four, or five atoms of oxygen respectively. A compound intermediate between a mon-oxide and a di-oxide is termed a sesqui-oxide. Where only two marked oxides are found, as in the case of tin, iron, copper, and mercury, the Latin or English name is often used with the termination of "ous," for the compound containing the least quantity of oxygen, and "ic" for that containing the most, thus :—

Tin gives stannous oxide ( $\text{SnO}$ ), stannic oxide ( $\text{SnO}_2$ ).

Iron gives ferrous oxide ( $\text{FeO}$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ).

Copper gives cuprous oxide ( $\text{Cu}_2\text{O}$ ), Cupric oxide ( $\text{CuO}$ ).

Mercury gives mercurous oxide ( $\text{Hg}_2\text{O}$ ), Mercuric oxide ( $\text{HgO}$ ).

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## CHAPTER III.

### METRIC SYSTEM OF WEIGHTS AND MEASURES

BEFORE proceeding further, it will be advisable to discuss the system of weights and measures now almost universally adopted in scientific investigation, and a short account of the physical properties of gases will subsequently form a suitable commencement to the study of the individual properties and modes of preparation of the various gaseous elements.

The English system of weights and measures in use for commercial purposes, and also used up to within a comparatively short time back for purposes of scientific investigation, is for many reasons unsatisfactory. Several separate systems are in use for different purposes; there is no even relation between the various degrees of each system, and there is likewise no direct and simple ratio between *weight* and *volume*. By a recent Act of Parliament,\* the use of the French system of weights and

\* 27th and 28th Vict., cap. 117, 27th July 1864.

measures, known as the Metric System, has been rendered legal; and although not yet adopted for commercial purposes, it is now almost universally used in scientific investigations in all countries. The advantages of the system are twofold: firstly, it is a decimal one; and, secondly, there is a simple and direct relation between weight, measure, and volume. The starting-point of the system is the metre, which was intended to be a measure having a direct relation to the earth's circumference, viz., one ten-millionth part of the distance from the equator to the pole. Subsequent experiments have proved that the original measurement was not quite correct. This is, however, of little consequence, as the actual unit measure in the form of a bar of metal, together with several accurate copies, have been preserved. The metre is equal to 39·37 English inches, and is divided into tenths, hundredths, and thousandths, called respectively decimetres, centimetres, and millimetres. It is also multiplied into successive quantities, known as decametres, hectometres, and kilometres.

The simple relation of the successive degrees of the system will be better seen as follows:—

*Table.*

10 Millimetres	= 1 Centimetre
10 Centimetres	= 1 Decimetre
10 Decimetres	= 1 Metre
10 Metres	= 1 Decametre
10 Decametres	= 1 Hectometre
10 Hectometres	= 1 Kilometre
10 Kilometres	= 1 Myriometre

Measures of area (square measure) are derived from the above measures of distance, as well as those of capacity (*cubic measure*); thus we have for area square metres, *decimetres, etc.*, and for capacity cubic metres, cubi

decimetres, etc. The cubic decimetre is also known as the litre. The relation between weight and capacity is further carried out by the adoption as a unit weight of one cubic centimetre of pure distilled water at its maximum density ( $4^{\circ}$  centigrade). This weight is called a Gramme, abbreviated in English into Gram (the gram weighs 15.4323487 English grains). This unit of weight, like the unit of measure, is divided into tenths, hundredths, and thousandths, known as decigrams, centigrams, and milligrams, and is decimally multiplied to give the larger weights.

*Table*

10 Milligrams	= 1 Centigram
10 Centigrams	= 1 Decigram
10 Decigrams	= 1 Gram
10 Grams	= 1 Decagram
10 Decagrams	= 1 Hectogram
10 Hectograms	= 1 Kilogram

#### MEASUREMENT OF TEMPERATURE. THERMOMETERS

All bodies are found to expand by heat, and to contract by cold. This fact is utilised for the measurement of changes of temperature by the construction of suitable apparatus, by which the degree of such expansion or contraction can be accurately measured. Liquids are most adapted for the purpose, as the expansion of solids is generally extremely small, whereas in gases it is inconveniently great. Of all the various known liquids, mercury is that which is most suited for the measurement of temperatures, by reason of its high boiling-point and low freezing-point. The range of measurement obtainable by a mercurial thermometer is thus very great. In the case of very low temperatures alcohol is usually employed, as this liquid has *never been frozen*; and where very minute variations

of temperature have to be measured, air thermometers are generally used. The mode of making a mercurial thermometer is as follows:—A straight piece of glass tubing, having a small and uniform bore, has a small bulb blown at one end, and the tube and bulb are then filled with mercury; the whole is then heated up to the highest temperature which the thermometer is required to register, and whilst still hot, the open end is hermetically sealed by fusing the tube by means of a blow-pipe flame. The next proceeding is the graduation of the instrument; for this purpose it is first plunged into melting ice, and when the mercury becomes stationary, the point on the tube to which it has sunk is marked. The thermometer is next immersed in the steam given off from water which is being boiled in a metallic vessel, and the height to which the mercury rises is then marked. Two points are thus obtained, the higher of which represents the boiling-point of water, and the lower the freezing-point. The intermediate space is then divided into equal parts, which are called *degrees*, the whole series being termed a *thermometric scale*. Three of these scales are in use, viz., Centigrade, Reaumur, and Fahrenheit. In the Centigrade scale the space between the boiling and freezing points is divided into 100 degrees, and in the Reaumur into 80. Below the freezing-point and above the boiling-point the graduation is continued in divisions of the same size, those below the freezing-point being characterised by a minus sign; thus,  $-1^{\circ}$ ,  $-2^{\circ}$ , etc. In the Fahrenheit scale the graduation is somewhat different. Fahrenheit plunged his thermometer into a mixture of ice and salt, and under the impression that he had produced the lowest attainable degree of cold, started with that point as a zero, dividing the space between the zero and the boiling-point into  $212^{\circ}$ . By this scale water freezes at  $32^{\circ}$ ; the zero of Fahrenheit's scale is therefore  $32^{\circ}$  below the freezing-point of water, and any lower temperature has to be distinguished by a minus

The Centigrade scale is used most extensively on the Continent, and as it is the most simple for purposes of scientific investigation, it will be used throughout the present work. The Reaumur scale is used in Russia and Sweden, while in England the Fahrenheit scale is that most in use for ordinary purposes.

The relation between the three scales—Reaumur, Centigrade, and Fahrenheit—is expressed by the numbers 4, 5, and 9. The following rules will be found useful in the mutual conversion of the one into the other:—

To convert Centigrade or Reaumur into Fahrenheit, multiply by 9, divide by 5 or by 4 respectively, and add 32.

To convert Fahrenheit into Centigrade or Reaumur, subtract 32, then multiply in the first case by 5, and in the other by 4, and subsequently divide by 9.

The following examples will serve as illustrations of the above rules:—

1. Required the equivalent in Fahrenheit of 25° Centigrade.

$$\frac{25 \times 9}{5} = 45 \quad \text{Answer, } 45 + 32 = 77^\circ \text{ F.}$$

2. Required the equivalent in Fahrenheit of 22° Reaumur.

$$\frac{22 \times 9}{4} = 49.5 \quad \text{Answer, } 49.5 + 32 = 81.5^\circ \text{ F.}$$

3. What is the equivalent in Centigrade of 190° Fahrenheit?

$$190 - 32 = 158 \quad \frac{158 \times 5}{9} = 87.7. \quad \text{Answer, } 87.7^\circ \text{ C.}$$

4. What is the equivalent in Reaumur of 148° Fahrenheit?

$$148 - 32 = 116 \quad \frac{116 \times 4}{9} = 51.5. \quad \text{Answer, } 51.5^\circ \text{ R.}$$

5. What is the equivalent in Centigrade of  $10^{\circ}$  Fahrenheit?

$$10 - 32 = -22 \quad \frac{-22 \times 5}{9} = -12^{\circ} \cdot 2 \quad \text{Ans., } -12^{\circ} \cdot 2 \text{ C.}$$

6. What is the equivalent in Fahrenheit of  $-10^{\circ}$  Centigrade?

$$\frac{-10 \times 9}{5} = -18 \quad -18 + 32 = 14 \quad \text{Answer, } 14^{\circ} \text{ C.}$$

Care must be taken, in examples similar to the last two given, to preserve the distinction between *plus* and *minus* signs.

## CHAPTER IV.

### PHYSICAL PROPERTIES OF GASES

#### RELATION TO TEMPERATURE

WHILST solid and liquid substances have very varying rates of expansion and contraction, which are in all cases comparatively small, all gases simple or compound expand or contract in the same proportion for equal increments or decrements of heat, such expansion and contraction being relatively great. Careful experiments have shown that one volume of a gas at  $0^{\circ}$  Centigrade increases by 0.003665 for every degree of increased temperature. This number is termed the *co-efficient of the expansion of gases*, and corresponds to  $\frac{1}{273}$  part, so that

273	volumes of gas at $0^{\circ}$ C. become
274	1° "
275	2° "
285	12° "

*The measurement of gases constitutes an important branch of chemical enquiry, and all gaseous volumes*

are corrected by calculation to  $0^{\circ}$  Centigrade, which is termed *the Standard temperature*. The method employed in effecting the requisite calculation is best illustrated by a few examples. The following formula may be used :—

$$\begin{array}{ll} V = \text{old volume} & t = \text{old absolute temperature} \\ V' = \text{new volume} & t' = \text{new absolute temperature} \\ \text{then } V' \times t = V \times t' \end{array}$$

To get new volume

$$V' = \frac{Vt'}{t} \quad \text{or} \\ t : t' :: V : V'$$

But it ought to be observed that the old volume multiplied by the new (absolute) temperature is equal to the new volume multiplied by the (absolute) temperature. In all cases 273 must be added to  $t$  or  $t'$  to express the absolute temperature. Suppose, for instance, it is required to know what volume 50 cubic centimetres of gas at  $100^{\circ}$  C. will become at  $0^{\circ}$  C. Now, as 273 volumes of gas at  $0^{\circ}$  C. will become 373 at  $100^{\circ}$ , so, conversely, 373 volumes at  $100^{\circ}$  would be reduced to 273 at  $0^{\circ}$ ; and the sum is therefore expressed as follows :—

$$373 : 273 :: 50 : x \\ x = 36.59$$

Again, let us assume that it is required to find out what volume 50 cubic centimetres of gas at  $0^{\circ}$  would become at  $100^{\circ}$ : then

$$273 : 373(273 + 100) :: 50 : x \\ x = 68.31$$

Assuming a third case: let it be required to ascertain what volume the 50 measures at  $10^{\circ}$  would become at  $30^{\circ}$ : then the proportion is stated thus :—

$$283(273 + 10) : 303(273 + 30) :: 50 : x \\ x = 53.53$$



## RELATION OF GASES TO PRESSURE

## THE BAROMETER

Liquids and solids are both to a certain extent reduced in bulk on being subjected to pressure, but the amount of such reduction is in all cases comparatively small; gases, on the contrary, undergo a very large reduction in volume on being subjected to pressure, and corresponding increase in bulk on the pressure being reduced. The contraction and expansion of gases under the influence of increased and diminished pressure is subject to a law known as the law of Boyle and Mariotte, from the names of its discoverers, and which may be expressed as follows:—*The volume of a gas is inversely proportional to the pressure to which it is subjected.* Thus, supposing at a pressure of 10 we have a volume of 100, if the pressure be halved—that is to say, reduced to 5—the volume is doubled, and becomes 200; if, on the other hand, the pressure is doubled, the volume is halved. In the same way, ten times the pressure reduces the volume to one-tenth of the original bulk, while at one-tenth the initial pressure the volume is increased tenfold. Gaseous pressure is measured by the barometer. This instrument, in its simplest form, consists of a glass tube of uniform bore, and having a length of about 33 inches. The tube is filled with mercury, previously freed from air by boiling, and inverted, the open end being immersed in a small cup filled with the same material. The mercury in the tube is then found to sink down slightly, finally leaving a column of about 30 inches in height. This represents the ordinary atmospheric pressure, which equals 14.7 lb per square inch. Fluctuations in the pressure of the atmosphere produce corresponding variations in the height of the mercurial column; and in order to observe these variations a scale is placed at the upper part

rometer tube, so that the exact level of the y can be observed. This scale is sometimes in sometimes in millimetres; but the latter division is now almost always employed for instruments used for scientific purposes. From the observations that have been made with regard to the relation between volume and pressure, it will be obvious that the observed volume of a gas will vary according to the corresponding variations of atmospheric pressure, and is therefore necessary to observe the height of the barometer when we are measuring the volume of a gas, and to fix upon some standard of pressure to which it is corrected. This *standard pressure* is that of 760 millimetres of mercury, the standard temperature is  $0^{\circ}$  Centigrade. When, for instance, it is mentioned that a certain amount of material will give a certain volume of gas, it is always understood that such volume is measured at, or corrected to, the standard temperature and pressure. In order to familiarize the student with the method of correcting volumes of gases for temperature and pressure, several examples are given.

A general rule for pressure correction may be expressed as follows:—*As the desired pressure is to the old pressure, so is the observed volume to the corrected volume*; or, in other words, the old volume multiplied by the old pressure is equal to the new volume multiplied by the new pressure. Thus, let

$$\begin{aligned} P &= \text{old pressure} & V &= \text{old volume} \\ P' &= \text{new pressure} & V' &= \text{new volume} \\ P \times V &= P' \times V' \end{aligned}$$

To get the new volume

$$V' = \frac{PV}{P'}$$

$$\text{or, } P' : P :: V : V'$$

*Example 1.* A volume of gas measures 120.4 CC. at

750 mm. pressure; what will be its volume at the standard pressure of 760 mm.?

$$760 : 750 :: 120.4 : x$$

$$x = 118.81$$

2. What would be the corrected volume of the 120.4 CC. if the observed pressure was 768 mm.?

$$760 : 768 :: 120.4 : x$$

$$x = 121.66$$

In correcting a volume of gas for both temperature and pressure, the correction for the one may be first made, and then the correction for the other on the number so obtained. Thus:—

3. What volume would 125 CC. of a gas at 766 mm. pressure, and at a temperature of 15° C., occupy when corrected to the standard temperature and pressure?

Taking the pressure correction first—

$$760 : 766 :: 125 : x$$

$$x = 125.9$$

$$288(273 + 15) : 273 :: 125.9 : x$$

$$x = 119.3, \text{ the corrected volume}$$

4. Again: What volume would the 125 CC. at 766 mm. and 15° C. occupy at 750 mm. and 50° C.?

Taking the pressure correction first, it is obvious that at the diminished pressure the volume would be increased; the sum is therefore stated thus:

$$750 : 766 :: 125 : x$$

$$x = 127.6$$

$$288(273 + 15) : 323(273 + 50) :: 127.6 : x$$

$$x = 143.1, \text{ the desired volume}$$

The two calculations may be made together, if desired; for instance, Example 3 may be expressed thus:

$$\frac{125 \times 766 \times 273}{760 \times 288} = 119.3, \text{ the answer.}$$

In like manner Example 4 may be calculated :

$$\frac{125 \times 766 \times 323}{750 \times 288} = 143.1, \text{ the answer.}$$

#### DIFFUSION AND EFFUSION OF GASES

Besides the physical properties of gases with relation to temperature and pressure, there is another property by virtue of which they have the power, when placed together, of becoming intimately mixed, notwithstanding great differences in density. This peculiarity of gases is known as *diffusion*, and it is regulated by a law which shows that a singular relation exists between the *diffusive power* of different gases and their *densities*. It has been found that *the velocity of diffusion of different gases is inversely proportional to the square roots of their densities*. A very good example of the different rates at which gaseous diffusion takes place, may be seen by fixing a thin plate of some porous substance, such as "Plaster of Paris," into one end of a piece of wide glass tube : if the tube is then filled with hydrogen, and its open end immersed in water, the water will be found to steadily rise in the tube up to a certain point with sufficient rapidity to be clearly perceptible; this circumstance is due to the fact that the lighter hydrogen passes out through the porous plate at a quicker rate than the heavier atmospheric air passes in ; that the air is passing into the tube as well as the hydrogen is passing out, is proved by examining the contents of the tube at the conclusion of the experiment, when no trace of hydrogen will be found, the whole of the gas having escaped and been replaced by air. There is no doubt that the diffusive properties of gases exercise an important function in the economy of nature. It is to a great extent due to gaseous diffusion, assisted by air currents arising from inequalities of temperature, that the composition of the atmosphere is

found so constant, and that the air of large cities which is being so continually polluted from organic exhalations and poisonous gases, is found to differ very little from the air of the open country.

*Effusion.*—This term is applied to the phenomena attending the passage of gases through a minute orifice in an exceedingly thin plate of metal. The law of effusion is the same as that of diffusion. Effusion has been used as a rapid means of ascertaining the density of gases by taking the *time* occupied by equal volumes of the respective gases at a given pressure in passing through a minute orifice in a thin metal plate. These times are called *effusion rates*.

#### RELATION OF VOLUME TO DENSITY IN GASES

A very simple relation has been found to exist between the *volumes* of gases entering into combination with each other. By the law of Avogadro, *equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules*. It follows, therefore, that *the densities of all the elementary bodies in the gaseous condition are the same as their respective atomic weights*, or the atoms of all the elements in the gaseous state occupy the same space. This is the expression of a general law, to which, however, there are a few notable exceptions, to which attention will be directed in the proper places. Thus the density of hydrogen is 1, that is, the same as its atomic weight; in like manner the density of chlorine is 35.5, that of nitrogen 14, and that of oxygen 16, and of bromine vapour 80. If, therefore, we know the weight of a given volume of hydrogen at a given temperature and pressure, the weight of an equal volume of any other elementary body in the gaseous state and under the same conditions, can be easily *calculated*. The weight of one litre of hydrogen at a pressure of 760 millimetres of mercury, and at a temperature

of 0° Centigrade, has been found to be 0·08936 gram. The weight, therefore, of an equal volume of any other simple gas is then found as follows:—

1 litre of chlorine weighs	$0\cdot08936 \times 35\cdot5 = 3\cdot172$	grams.
„ nitrogen „	$0\cdot08936 \times 14 = 1\cdot251$	grams.
„ oxygen „	$0\cdot08936 \times 16 = 1\cdot430$	grams.
„ bromine vapour „	$0\cdot08936 \times 80 = 7\cdot149$	grams.

In like manner the weight of an equal volume of any other element in the gaseous state can be calculated from its known density.

In the case of compounds, it has been proved that *the density of a compound gas is one-half its molecular weight*; that is to say, that a molecule of a compound gas occupies the same space as two atoms of hydrogen. This law has likewise a few exceptions, which, however, are believed to be more apparent than real, and they will receive attention under their respective headings.

The law just enunciated is the direct sequence of the known facts of combination by volume, for it has been found that no matter how many volumes of different gases unite together to form gaseous compounds, that the volume of the product always occupies the same space as two atoms of hydrogen; thus, one volume of oxygen weighing 16, and two volumes of hydrogen weighing 2, unite to form *two* volumes of water vapour weighing 18; one volume of nitrogen weighing 14, and three volumes of hydrogen, unite to form two volumes of gaseous ammonia weighing 17; one volume of chlorine weighing 35·5 unites with one volume of hydrogen to form two volumes of hydrochloric acid weighing 36·5; one volume of carbon vapour weighing 12 unites with four volumes of hydrogen to form two volumes of marsh gas weighing 16. As in each of these cases the product occupies the same space as *two* atoms of hydrogen, the *density*, which is the weight of a bulk of the gas equal to *one* volume of hydrogen, must necessarily be one-half, and we therefore obtain

the general law that *the density of a compound gas is one-half of its molecular weight.*

To obtain the weight, therefore, of a litre of any compound gas at the temperature of  $0^{\circ}$  centigrade, and under a pressure of 760 millimetres of mercury, we have simply to multiply the weight of a litre of hydrogen 0.08936 gram by one-half the molecular weight,—thus

1 litre of water vapour	= $0.08936 \times 9 = .8042$ gram
„ ammonia	= $0.08936 \times 8.5 = .7595$ gram
„ hydrochloric acid	= $0.08936 \times 18.25 = 1.6308$ grams
„ marsh gas	= $0.08936 \times 8 = .7148$ gram

It will be seen that an experimental determination of gaseous density may thus be made a means of determining molecular weight. The method is, in fact, extremely useful for this purpose, as will be seen when we come to the portion of the work treating of organic chemistry.

In calculations bearing on the relation between weight and volume of gases, in place of taking as unit the weight of one litre of hydrogen at the standard temperature and pressure, the volume occupied by one gram of hydrogen is sometimes taken, viz., 11.19 litres. The weight of the same volume of any other gas is obviously as its density, thus—

11.19 litres of H	weigh 1 gram
11.19 „ O	„ 16 grams
11.19 „ Br	„ 80 „
11.19 „ HCl	„ $18.25 (36.5 \div 2)$

The following examples will serve as practical examples of calculations of the relation between volume and density in gases:—

1. What volume in litres would 10.34 grams of oxygen occupy at the standard temperature and pressure?

*Now, 11.19 litres of oxygen weigh 16 grams, and conversely, therefore, 16 grams measure 11.19 litres.*

$$16 : 10.34 :: 11.19 : x$$

$$x = 7.23 \text{ litres}$$

If the weight of a litre of hydrogen is taken as the basis of calculations, the weight of a litre of oxygen is  $0.08936 \times 16 = 1.43$  grams.

$$1.43 : 10.34 :: 1 : x$$

$$x = 7.23 \text{ litres}$$

2. What is the weight of 9.4 litres' measure of chlorine at the standard temperature and pressure?

As 11.19 litres weigh 35.5 grams,

$$11.19 : 9.4 :: 35.5 : x$$

$$x = 29.82 \text{ grams}$$

3. What volume in litres will 10 grams of hydrochloric gas occupy at the standard temperature and pressure?

Molecular weight of  $\text{HCl} = 36.5$ , density one-half— $18.25$ ;  $18.25$  grams of  $\text{HCl}$  would occupy, therefore, the same space as one gram of  $\text{H}$ , viz.,  $11.19$  litres. Then

$$18.25 : 10 :: 11.19 : x$$

$$x = 6.09 \text{ litres}$$

Where it is desired to calculate the relation between the volume and the density of a gas under conditions of temperature and pressure different from the standard, the calculation is effected thus:—

4. What volume will 10 grams of nitrogen occupy at  $20^\circ \text{C}$ . and  $760 \text{ mm}$ .?

Firstly, find what is the volume of the 10 grams at the standard temperature and pressure,

$$14 : 10 :: 11.19 : x$$

$$x = 7.99 \text{ litres}$$

And  $7.99$  litres at  $0^\circ$  and  $760 \text{ mm}$ . =  $8.57$  litres at  $20^\circ \text{C}$ . and  $760 \text{ mm}$ .



5. A volume of nitrogen measures 10 litres at 752 mm. and 15° C., what will it weigh at the standard temperature and pressure?

10 litres at 752 and 15° = 9.38 litres at 760 mm. and 0° C., and as 11.19 litres of N weigh 14 grams,

$$11.19 : 9.38 :: 14 : x$$

$$x = 11.7 \text{ grams}$$

## CHAPTER V.

### THE NON-METALLIC ELEMENTS

THESE will be discussed in the following order:—

OXYGEN	SULPHUR
HYDROGEN	SELENIUM
NITROGEN	TELLURIUM
CHLORINE	CARBON
BROMINE	SILICON
IODINE	BORON
FLUORINE	PHOSPHORUS

### OXYGEN

SYMBOL, O

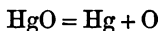
COMBINING WEIGHT, 16

Oxygen derives its name from “�ξύς,” acid, and “γεννάω,” I produce, by reason of an old conception that its presence was essential to the formation of all acid bodies. This belief is now known to be incorrect. It was discovered in 1774 by Scheele in Sweden, and independently by Priestly in the same year in England.

DISTRIBUTION.—Oxygen is a very abundant element *existing in the free state in atmospheric air, of which*

it forms one-fifth by volume, and in the combined condition constituting eight-ninths by weight of water, besides being a large constituent of the crust of the earth in combination with various other elements.

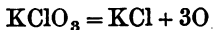
**PREPARATION.**—Although the atmosphere is a vast store-house of free oxygen, its separation from the nitrogen with which it is mixed is attended with many practical difficulties, and it is therefore found more convenient to prepare the gas from some of its compounds. Many of these compounds may be readily used for the preparation of oxygen, and among them may be mentioned mercuric oxide,  $\text{HgO}$ , manganese dioxide,  $\text{MnO}_2$ , and potassium chlorate,  $\text{KClO}_3$ . Other modes of preparing oxygen on a larger scale will be found under Sulphuric Acid, Barium Dioxide, and Manganese. Mercuric oxide was first used by Priestly for the preparation of oxygen. When this substance is heated in a tube it splits up into its constituent elements, the oxygen passing off as a gas, and the mercury condensing in silvery metallic globules on the side of the tube.



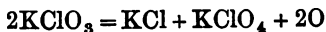
From manganese dioxide oxygen is prepared by submitting it to a red heat in an iron gun-barrel, or other suitable receptacle. The following equation represents the reaction which occurs:—



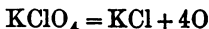
Potassium chlorate subjected to heat fuses to a clear liquid, evolves oxygen, and leaves potassium chloride, thus—



The reaction really occurs in two stages, in the first of which potassium chloride and potassium perchlorate are formed with evolution of a small quantity of oxygen, thus—



and in the second stage the potassium perchlorate is decomposed as follows :—



The production of oxygen from potassium chlorate is much facilitated by mixing the powdered salt with a little manganese di-oxide before applying the heat. The manganese di-oxide suffers no change during the reaction, and can be recovered unaltered at the conclusion of the experiment.

Of the three methods of procuring oxygen which have been quoted, the last is that by which the gas may be most readily and abundantly obtained in a pure state. The first method mentioned is only useful as an illustrative experiment, while manganese di-oxide is used as a source of oxygen, when a comparatively cheap method of procuring the gas is required, without reference to special purity.

Knowing what takes place in the preparation of oxygen from the different materials given, it is easy to calculate how much of each material must be taken in order to obtain a given weight or volume of the gas, or conversely what weight or volume of gas can be procured from a given weight of material. Thus, supposing it is required to ascertain how much potassium chlorate must be taken to give 100 grams of oxygen: by the equation  $\text{KClO}_3 = \text{KCl} + \text{O}_3$ , it is shown that one equivalent of  $\text{KClO}_3 = 122.6$  ( $\text{K} = 39.1$ ,  $\text{Cl} = 35.5$ ,  $\text{O}_3 = 48$ ) yields three equivalents, or 48 ( $16 \times 3$ ) of oxygen; 48 parts of oxygen are therefore obtained from 122.6 parts of  $\text{KClO}_3$ , and in order to find out how much  $\text{KClO}_3$  must be taken to yield 100 grams of oxygen, we have the simple rule of three sum.

$$\begin{array}{ccccccc} 48 & : & 100 & :: & 122.6 & : & x \\ & & & & x = 255.4 \text{ grams.} \end{array}$$

*If it is required to ascertain how much  $\text{KClO}_3$  must be taken to obtain a given volume of oxygen, say*

100 litres, we must first find out the weight of 100 litres in grams, and then calculate the amount of  $\text{KClO}_3$  needed to produce the weight of oxygen so found. The weight of a litre of hydrogen at  $0^\circ\text{C}$ . and 760 mm. is 0.08936 grams; and as the density of oxygen is 16—that is to say, that one litre of oxygen is sixteen times heavier than the corresponding volume of hydrogen—the weight of one litre of O will be  $0.08936 \times 16 = 1.42976$  grams, and the weight of 100 litres will be  $1.42976 \times 100 = 142.976$  grams. In order to find the amount of  $\text{KClO}_3$  necessary to produce this weight of oxygen we have the sum—

$$48 : 142.976 :: 122.6 : x$$

$$x = 365.1 \text{ grams, } \text{KClO}_3$$

to give 100 litres of oxygen at the standard temperature and pressure.

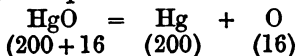
Again, supposing it is asked what weight or volume of oxygen can be obtained from a given quantity of  $\text{KClO}_3$ , say 100 grams, the *weight* is first ascertained thus—

$$122.6 : 100 :: 48 : x$$

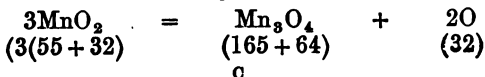
$$x = 39.1 \text{ grams.}$$

The *volume equivalent* in litres is then ascertained by dividing the 39.1 grams by the weight of a single litre, thus:  $39.1 \div 1.429 = 27.36$  litres.

In the same way may be calculated the amount of oxygen obtainable from any given weight of mercuric oxide, taking the equation—



as a basis in which 216 parts of HgO yield 16 parts of O. The quantity of oxygen which can be obtained from a given weight of manganese di-oxide can also be calculated in the same way from the equation—



in which three equivalents of  $\text{MnO}_2 = 261$  yield two equivalents, or 32 parts, of oxygen.

The mode of procuring oxygen from potassium chlorate, and of subsequently collecting the gas for experiment, will serve as a typical example of the mode of manipulating gases generally. We shall therefore describe the method usually adopted. The mixture of potassium chlorate and manganese di-oxide is introduced into a glass flask (an ordinary Florence oil flask, previously cleaned and dried, will answer the purpose); one end of a bent glass tube is then connected with the neck of the flask by means of a perforated cork, the other end of the tube dipping beneath the surface of some water contained in a pneumatic trough. A retort may also be used for the purpose, as

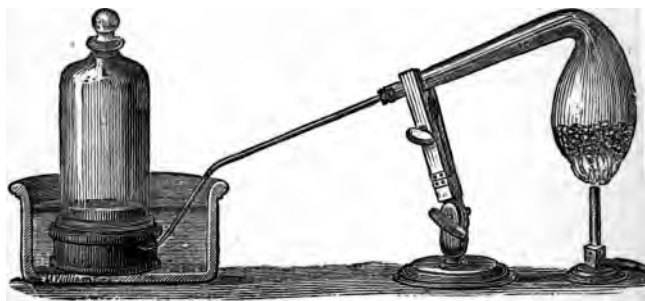


Fig. 1

shown in the annexed diagram. The pneumatic trough is fitted with a shelf, upon which may be placed either one or a series of inverted wide-mouthed stoppered glass bottles previously filled with water. Everything being prepared, heat is applied to the flask or retort containing the potassium chlorate. After a short time oxygen gas is evolved. The first portions of the gas should be *allowed to escape*, as they are contaminated with air.

When it is judged that all the air in the flask has been expelled, and that, consequently, the oxygen is passing in a pure condition from the extremity of the outlet-tube which dips beneath the water-covered tray in the pneumatic trough, a bottle may be placed so that the gas passes into it. The tray is pierced with holes, or better still, small inverted funnels are so fixed on the under surface of the tray that a bottle may be placed over each. The oxygen finds its way into the bottle in large bubbles, the water becoming gradually displaced. When the bottle is full of gas it may be carefully removed from the tray, and while the mouth is still under water the stopper inserted, and the bottle can then be removed for experiment. Other bottles may then be filled in a similar way. The method of collection above described serves for all gaseous bodies which are not soluble to any extent in water. For the manipulation of gases which are absorbed by water, and which have no action on mercury, a trough filled with the liquid metal is used, and so made as to require the employment of a comparatively small quantity of mercury. Mercurial troughs are also used in the analysis of those gases which have to be examined in a perfectly dry condition, and where great accuracy is required.

Another mode for the collection of gases for ordinary experimental purposes is by displacement, but this method is only applicable in cases of gases which are lighter or heavier than atmospheric air. In the first case, the vessel to be filled is placed in an inverted position over the tube from which the gas is issuing, when the air is gradually displaced. In the second case, the tube from which the gas is flowing is carried to the bottom of the vessel to be filled, the latter being in its usual position.

**PROPERTIES.**—Oxygen, together with nitrogen and hydrogen, were regarded, up to a comparatively recent period, as absolutely permanent gases, having been sub-

jected to a pressure of 3000 atmospheres without becoming liquified. It appears, however, that by the employment of extreme pressure, conjointly with great cold, Messrs Cailletet and Raoul Pictet have recently succeeded in effecting the liquifaction of oxygen and hydrogen. The pressure used amounted to from 550 to 650 atmospheres, the temperature being  $120^{\circ}$  to  $140^{\circ}$  below zero. At ordinary temperatures and pressures oxygen is a colourless, odourless, invisible gas ; it is the great supporter of combustion and of animal life ; by its presence in the atmosphere fires and furnaces are able to burn, gas, oil, and candles to afford light, and life is maintained. Any substance which burns in the air, burns with increased energy in oxygen ; thus a small chip of wood which has been ignited, and the flame from which has been blown out, leaving only a red glowing end, bursts suddenly into flame when plunged into oxygen. The test is characteristic of the presence of the gas. A taper or candle is relighted by the same treatment. A piece of ignited charcoal immersed in a jar of oxygen burns with great brilliancy, sometimes throwing off the most beautiful scintillations. The effect is most striking when a piece of bark charcoal is used. If a small fragment of ignited charcoal or wood be attached to the end of a piece of thin iron wire and introduced into oxygen, the organic material is first consumed, and the metal itself subsequently catches fire and burns brilliantly, throwing off sparkling scintillations, and every now and then drops of fused oxide of iron fall from the burning wire in such an intensely heated condition as to firmly attach themselves to the bottom of the glass bottle, even if covered with as much as half an inch of water. Sulphur burns in oxygen with a fine blue flame, while phosphorus, under the same conditions, gives a white light of the most dazzling brilliancy. In all the cases of combustion which have been mentioned, the phenomena have been those of energetic oxidation and *combination of oxygen* with the respective substances used

has taken place, oxides being formed with evolution of heat and light. The contents of the jars after the combustion may be examined by appropriate tests. That in which the charcoal was consumed, for instance, will contain carbonic acid, which can be proved by introducing a little clear lime water into the jar and shaking up, when a white precipitate will take place from the union of the lime, and the carbonic acid to form calcium carbonate (or chalk). The jar in which the sulphur was consumed contains sulphurous acid, which can be proved by the peculiar smell of burnt sulphur, and by introducing a piece of blue litmus paper previously moistened, which will be first reddened and then bleached. The combustion of the phosphorus also affords an acid body, viz., "phosphoric acid," while the iron is converted into an oxide having the composition  $\text{Fe}_3\text{O}_4$ .

The power which oxygen possesses of supporting animal life is also an example of oxidation, by which the carbonaceous compounds of the blood are oxidised in the lungs by the inspiration of atmospheric air, carbonic acid and water being formed. It is by this process continually going on that animal heat is maintained, and the blood maintained in a healthy condition. The presence of carbonic acid in the breath may be easily proved by blowing through a glass tube into a little clear lime water, when the solution soon becomes turbid from the formation of finely divided calcium carbonate. In the economy of nature plants and animals exercise an entirely opposite action on the atmosphere, for while the latter are continually withdrawing oxygen and giving out carbonic acid, the function of vegetation is to decompose the carbonic acid, exhaling oxygen, and retaining the carbon for the purpose of building up of their tissues. This decomposition proceeds slowly in ordinary diffused daylight, but is *most active* in actual sunshine.

*Oxygen is best absorbed from any gaseous mixture containing it by means of an alkaline solution of*



potassium pyrogallate; hydrated ferrous and manganous oxides also absorb it, and with nitric oxide it forms ruddy fumes of nitric peroxide.

**PRINCIPAL COMPOUNDS.**—All the elements with the single exception of fluorine unite with oxygen to form oxides, and the combinations which are very numerous and important will receive attention under the respective elements.

### ALLOTROPIC OXYGEN. OZONE

When oxygen is subjected to a series of electrical discharges it undergoes a peculiar modification of properties. The volume of gas becomes less, it acquires a peculiar smell, and is able to effect oxidations under circumstances in which common oxygen has no action. To this peculiar allotropic form of oxygen the term ozone has been applied.

Ozone is oxygen in a condensed form, three volumes of oxygen forming two of ozone, so that the density of the one is half as much again as that of the other. By exposure to a temperature of between  $250^{\circ}$  and  $300^{\circ}$  it is changed into ordinary oxygen. Ozone is formed in small quantity during the electrolytic decomposition of water, and can also be obtained by the action of strong sulphuric acid on potassium permanganate, and by the action of phosphorus on moist air. Whichever process is used for the preparation of ozone, the product is never pure, but is simply ozonised oxygen, that is to say, ordinary oxygen containing a small percentage of ozone. By the action of electrical discharges on oxygen it is possible to diminish the volume of the gas by about one-twelfth. In any given quantity of oxygen the whole of the gas cannot be transformed into ozone by the action of electricity, unless the ozone so produced is removed as fast as it is formed by the use of some absorbent agent, such, for instance, as potassium iodide.

## HYDROGEN

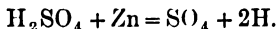
SYMBOL, H

COMBINING WEIGHT, 1

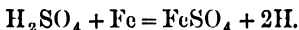
Derives its name from “*ὕδωρ*,” water, and “*γεννάω*,” I produce. Hydrogen was discovered by Paracelsus in the sixteenth century, but was not investigated until 1781, when its properties were first studied by Cavendish.

**DISTRIBUTION.**—Hydrogen occurs in nature mostly in combination with oxygen in the form of water, of which it constitutes one-ninth part by weight. It is also a constituent of the greater number of the substances used for the production of heat or light, and is present in most organic structures. It is only met with in the free state imprisoned in certain specimens of meteoric iron, and in the gases emanating from some volcanoes.

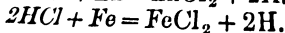
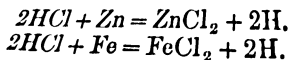
**PREPARATION.**—Hydrogen may be prepared by displacing it from some of its acid compounds such as sulphuric acid  $\text{H}_2\text{SO}_4$ , and hydrochloric acid  $\text{HCl}$ , or it may be obtained from the decomposition of water. The usual and most convenient process for obtaining hydrogen is from dilute sulphuric acid, by the action of zinc or iron; thus, zinc and sulphuric acid afford zinc sulphate and free hydrogen—



Iron, in like manner, yields ferrous sulphate and free hydrogen—



If hydrochloric be used in place of sulphuric acid, the action is very similar, with the exception that chlorides, instead of sulphates, are formed—

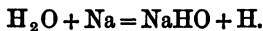


The following diagram shows the apparatus for the preparation of hydrogen. The metallic zinc or iron is placed in the larger bottle, the dilute acid is then added by the tube funnel, and the evolved gas is washed and rendered purer by passing through a little water in the

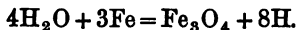


Fig. 2

smaller bottle. From water, hydrogen may be prepared by the action of an alkali metal, such as sodium, at the ordinary temperature, of iron at a red heat, or by electrolytic decomposition. By the first of these three methods half the hydrogen of the water is given off, the alkali metal being converted into hydrate ; thus,

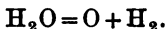


By passing steam over metallic iron heated to redness, decomposition ensues, with formation of magnetic oxide of iron, and liberation of hydrogen.



When the terminals of a galvanic battery are immersed *in water, which has been previously acidulated with a little sulphuric acid*, in order to render it a better con-

ductor of electricity, oxygen gas is evolved from the positive pole, while hydrogen is given off from the negative.



The method generally used for the preparation of hydrogen is by the use of zinc and dilute sulphuric acid, a glass flask being used, fitted with a cork having two perforations, through one of which is passed a tube for the delivery of the gas, while the other admits a tube funnel for pouring in the dilute acid. With a knowledge of the action that occurs in the preparation of hydrogen from the various sources named, it is easy to calculate the amount of material which must be taken to produce a given weight or volume of hydrogen. Supposing, for instance, we require to ascertain how much hydrogen (by weight) is evolved by the action of 100 grams of sodium on water. By the equation  $\text{Na} + \text{H}_2\text{O} = \text{NaHO} + \text{H}$ , one equivalent of sodium (23) yields one equivalent of hydrogen (1)—100 grams of sodium would yield therefore

$$\begin{array}{ccccccc} 23 & : & 100 & :: & 1 & : & x \\ & & & & x-4.347 & & \end{array}$$

The volume in litres corresponding to this weight may be obtained by dividing by the weight of one litre of hydrogen.

$$4.347 \div 0.08936 = 48.6 \text{ litres}$$

In the same way may be calculated the volume of hydrogen obtainable by the action on water of the alkali metals lithium, potassium, rubidium, and caesium. Again, supposing it is required to find how much zinc and sulphuric acid must be taken in order to procure a given quantity of hydrogen, such, for instance, as would fill a balloon having a capacity of 1000 litres, the temperature of the air being 15° and the barometer standing at 750 mm. We must first calculate the volume

of hydrogen at the standard temperature and pressure corresponding to 1000 litres at 15° and 750°; this is done as follows—

$$\frac{1000 \times 273 \times 750}{(273 \times 15) \times 760} = \frac{1000 \times 273 \times 750}{288 \times 760} = 935.4 \text{ litres}$$

As the weight of one litre of hydrogen at the standard temperature and pressure is 0.08936 grams, the 935.4 litres will weigh  $0.08936 \times 935.4 = 83.587$  grams. By the equation  $\text{H}_2\text{SO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{H}_2$ , one equivalent of  $\text{H}_2\text{SO}_4$  (98 parts) and one equivalent of zinc (65.2) yield two parts of hydrogen. To find therefore the amounts of zinc and sulphuric acid which must be taken to yield 83.587 grams of hydrogen, we have, taking sulphuric acid first,

$$\begin{array}{l} 2 : 83.587 :: 98 : x \\ x = 4095.7 \text{ grams } \text{H}_2\text{SO}_4 = 4.095 \text{ kilos;} \end{array}$$

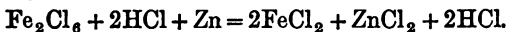
while to find the quantity of zinc, we have

$$\begin{array}{l} 2 : 83.587 :: 65.2 : x \\ x = 2724.9 \text{ grams } \text{Zn} = 2.725 \text{ kilos.} \end{array}$$

**PROPERTIES.**—Hydrogen is an invisible gas, without odour, taste, or colour. It is a non-supporter of combustion, but is very inflammable, burning in the air with a blue, non-luminous flame of intense heat, and yielding water as the sole product of combustion. Mixed with oxygen or air, hydrogen forms an explosive mixture, and care should therefore be taken not to apply a light to vessels in which the gas is being generated without previously allowing the air to be thoroughly expelled.

Hydrogen is the lightest substance known, a litre at 0° C. and 760 mm. weighing only 0.08936 gram, and a gram measures 11.19 litres. Hydrogen is taken as the unit of density for gases, all gaseous *densities being the weight as compared with an equal volume of hydrogen.* The chemical relations of hydro-

gen have been held to establish its resemblance to a metal, and Professor Graham has found that, on decomposing water by a galvanic current, metallic palladium being used as the negative electrode, the palladium absorbed 900 times its bulk of hydrogen, forming an alloy containing nearly single equivalents of each element. The specific gravity of the hydrogen in this alloy was found to be 1.95, and in this peculiar condition it is termed "Hydrogenium." Hydrogen sometimes acts as a reducing agent, more especially at the moment of its liberation from one of its compounds, in which condition it is spoken of as being in *the nascent state*. All elements are most chemically active when in this condition; that is, at the moment of their liberation from their respective compounds. A striking example of the difference in the chemical activity of ordinary free hydrogen and nascent hydrogen is exhibited in the action of each element under either of the above conditions on certain metallic solutions. Ferric chloride, for instance, in solution may be treated with ordinary hydrogen without becoming in any way changed, but when acted upon by nascent hydrogen, is rapidly reduced to ferrous chloride. The most convenient mode of acting on a solution by nascent hydrogen is by placing fragments of zinc in the solution previously rendered acid.



Hydrogen is sometimes employed for filling balloons, but coal-gas is now more generally used. It is also used for the oxyhydrogen blowpipe, in which a flame of the most intense heat is produced by burning a mixture of oxygen and hydrogen.

PRINCIPAL COMPOUNDS.—The most important compounds of hydrogen are its oxides, of which there are two, viz.—

Hydrogen monoxide, or Water,  $\text{H}_2\text{O}$ .

Hydrogen dioxide,  $\text{H}_2\text{O}_2$ .

**HYDROGEN MONOXIDE, WATER,  $H_2O$ .**—The composition of water was first shown by Cavendish in 1781, and he proved that it consisted of two volumes of hydrogen and one volume of oxygen. Cavendish took a strong dry vessel of glass provided with a stopcock. This vessel was thoroughly exhausted of air, and subsequently filled with a mixture of oxygen and hydrogen in the proportions already named, and the whole carefully weighed. The gases were then exploded by passing an electric spark, when water was seen to be deposited on the sides of the vessel, and a subsequent weighing proved the weight to be unaltered. The mouth of the vessel being then immersed in water, and the stopcock opened, the water rushed in and completely filled the space previously occupied by the mixed gases. Since the time of Cavendish the methods of gas analyses have been considerably improved, and in place of the form of vessel used by him, an instrument called the Eudiometer is employed, by which exact results may be obtained, and which enables the volume of gas to be determined with accuracy before and after experiment—a condition which is absolutely necessary in the present condition of general gas analysis. The Eudiometer, as now used, consists in its simplest form of a glass tube bent into the form of a U. One end of the tube so bent is left open, the other end being hermetically sealed. The sealed limb is graduated, and provided at its uppermost extremity with two platinum wires, fixed into the glass on opposite sides of the tube, with a space of about one-tenth of an inch between the points of the wires for the passage of an electric spark. The composition of water may be synthetically determined by the use of the Eudiometer in the following way:—The tube is first filled with mercury, and a quantity of hydrogen gas introduced. This is accomplished by closing the open *end of the tube* by the thumb, inserting the *instrument*, and dipping its extremities beneath the level of

some mercury in a mercurial trough. A tube, from which hydrogen gas is issuing, is then brought under the open extremity of the Eudiometer, and the gas ascends into the tube, and displaces some of the mercury. Sufficient gas having been thus admitted, the orifice of the tube is closed by the thumb, the tube itself removed from the mercurial trough, and, by a little manipulation, the gas which has been introduced is transferred to the closed limb of the tube. The Eudiometer being then brought into an upright position, and some of the mercury removed, so as to bring the surfaces of the liquid to a level in each limb of the tube, the exact volume of gas may be noted.

Let us suppose that a volume of hydrogen has been introduced in the manner described, and that the closed limb of the Eudiometer is divided into 100 divisions, the gas was found to occupy 26 of such divisions. About an equal volume of oxygen is then introduced into the tube in the same way that the hydrogen was admitted, and the volume again noted, with the same precautions as before. The open end of the Eudiometer is now tightly closed by the thumb, and an electric spark passed through the mixed gases, when explosion occurs, with production of a blue flame. The thumb is then removed, and the tube and its contents allowed to stand for some time, in order that the temperature may be reduced to that of the air; and, finally, the mercury is levelled, and the volume of the residual gas noted. This residual gas will prove on examination to be pure oxygen. We then have the following data:—

Hydrogen taken . . . . .	26 volumes
Total volume of gas after admission of oxygen . . . . .	51 „
Therefore, volume of oxygen used (51 - 26) = . . . . .	25 „
Volume of residual gas after explosion . . . . .	12 „



Therefore, oxygen which has disappeared by combination with hydrogen,  $(25 - 12) = \quad \quad \quad 13$  volume

We see, therefore, that 26 volumes of hydrogen have united with 13 of oxygen to produce water; that is, say, the two gases have combined in the proportion of two volumes of the latter to one of the former.\* accurate experiments a slightly different form of Eudiometer is preferable, consisting of a perfectly straight, graduated tube, sealed at the top, and with platinum wires fused into the closed end in the way previously described. It is held in a vertical position by means of a suitable stand, and its open end dips into a trough filled with mercury. A piece of caoutchouc is fixed at the bottom of the trough, on to which the open end of the tube is pressed during an explosion. Fig. 3 shows this form of Eudiometer. In all experiments on gases it must be remembered that accurate results can only be secured by observing the temperature of the gas, and also the pressure to which it is subjected at each stage of the manipulation, and making suitable corrections for any differences which may be observed.

The composition of water may also be determined synthetically by the use of copper oxide. This substance may be heated to redness in the air without change, but in the presence of hydrogen it becomes reduced to metallic copper, its oxygen uniting with the hydrogen to form water. The following experiment, based on the above reaction, may be made:—Into a bulb-tube of hard glass a quantity of dry copper oxide is introduced, and the whole is then carefully weighed. The tube is conne

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\* The volume occupied by the water produced is so small that it may be neglected. It only amounts to  $\frac{1}{1000}$ th part of the bulk of the mixed gases.

on the one side with an arrangement for generating pure dry hydrogen, and on the other side with some tubes containing dry calcium chloride, or fragments of pumice stone moistened with sulphuric acid. The weight of these latter tubes is carefully ascertained before the experiment. The bulb-tube and its contents are then heated to redness, and hydrogen allowed to pass, when the copper oxide loses oxygen, which unites with the hydrogen to form water; and the water so produced is carried forward in the state of vapour, and absorbed by the tubes provided for the purpose. The whole is then allowed to cool, and the tube containing the copper oxide, and those used for absorbing the aqueous vapour, weighed, when it will be found that for every 16 parts of oxygen lost by the oxide 18 parts of water have been absorbed by the calcium chloride or pumice. It is thus proved that water consists of one equivalent of oxygen and two of hydrogen, and its formula is, therefore,  $H_2O$ .

Attention has already been directed to the electrolytic decomposition of water as a means of procuring hydrogen, and the experiment may be well taken to illustrate the composition of water, for if a graduated tube filled with water be placed over each terminal of the galvanic battery, the terminals themselves being immersed in acidulated water, it will be found that for every single volume of oxygen collected in the one tube, a little more than double the amount of hydrogen accumulates in the other. The volume of hydrogen would be exactly double, were not this gas slightly less soluble in water than oxygen, and hence the apparent discrepancy.

The physical properties of water are so well known as to scarcely need description. In its perfectly pure condition it is a transparent fluid which is colourless, odourless, and tasteless. It evaporates when fully exposed to the air at all temperatures. It boils at  $100^\circ$ , *freezes at  $0^\circ$* , and attains its maximum density

at 4°. Water is a very powerful solvent, dissolves a very large number of substances, the solvent action in most cases, becoming greater with increase of temperature. The gases are also all more or less dissolved in water, but the amount of such solubility is very different; for while such substances as hydrogen, nitric oxide and oxygen are only taken up in very small quantities, hydrochloric acid and ammonia are absorbed to a great extent, whilst chlorine, carbon dioxide, and sulphur dioxide occupy intermediate places. It is to the solubility of oxygen and carbonic acid in water that animal life is capable of existence. The solubility of gases in water, unlike that of the majority of solids, is greater the lower the temperature.

The following table shews the volumes of various gases absorbed by one volume of water at different temperatures:—

NAME OF GAS	At 0°	At 10°	At 20°
Oxygen - - - -	0·041	0·033	0·025
Nitrogen - - - -	0·020	0·016	0·012
Hydrogen - - - -	0·019	0·019	0·019
Nitrogen monoxide - -	1·310	0·092	0·075
Carbon dioxide - - -	1·800	1·18	0·85
Chlorine - - - -	—	2·59	1·82
Sulphuretted hydrogen -	4·370	3·59	2·85
Sulphurous oxide - - -	53·90	36·40	27·1
Hydrochloric acid - - -	505·0	472·0	440
Ammonia - - - -	1180	898	700

Water may be obtained in a pure condition by boiling any variety of ordinary natural water to drive off the dissolved gases, and then distilling it; that is, boiling it in a suitable vessel, and condensing the steam evolved by passing it through a condenser. Water is found in nature in three distinct physical conditions; gas, *in the form of aqueous vapour or steam*; liquid

water generally so called, and solid as ice. Below  $0^{\circ}$  it is solid, between  $0^{\circ}$  and  $100^{\circ}$  liquid, and at temperatures above  $100^{\circ}$  gaseous. Liquid water, at a particular temperature, forms a singular exception to one otherwise almost universal law, viz., that bodies expand by heat and contract by cold. When water at the ordinary temperature of the air is gradually cooled down, it regularly contracts until the temperature reaches  $4^{\circ}$ . From  $4^{\circ}$  to  $0^{\circ}$  the liquid expands, and a further and considerable expansion occurs on the solidification of the water into ice. The peculiar property of water of *expanding* between  $4^{\circ}$  and  $0^{\circ}$  plays an important part in the economy of nature. During winter, the surface of all natural reservoirs of water becomes cooled, and the surface water acquires therefore an increased density, by reason of which it sinks and exposes a fresh layer of water to the cooling action of the air. This cooling process proceeds until the whole mass of water has become reduced to a temperature of  $4^{\circ}$ , when further cooling has simply the effect of rendering the surface water *lighter* than that underneath, so that ice is eventually formed, while the temperature of the great mass of water remains at  $4^{\circ}$ . If the water continued to contract until the freezing point was reached, the process of circulation described would continue to  $0^{\circ}$ , when the whole mass of water would suddenly solidify, our rivers and lakes would then become masses of ice, and all living creatures which they contained would be killed. Very large masses of water are seldom covered with ice in temperate countries, owing to the fact that the continuance and degree of cold are seldom sufficient to cool the whole body of water as low as  $4^{\circ}$ . The sudden expansion of water on freezing takes place with almost irresistible force, as is exemplified in nature by the fracture of rocks during frost. The chinks and crevices of the hard stone become filled with water, which subsequently freezes and the rock is thus split open. When a substance is capable, like

water, of the three physical states of solid, liquid, and gaseous, it is found that in order to effect a change from the one condition to the other, such as solid to liquid, a certain amount of heat is absorbed, and a further amount disappears during the passage of the liquid form into the gaseous. The heat, disappearing in this way, is termed "latent heat," and its amount is a perfectly fixed and constant quantity. The *latent heat of water* is 79 *thermal units*, a thermal unit being *the amount of heat required to raise a unit weight (1 kilogram) of water through one degree centigrade*. This may be demonstrated by mixing a kilogram of ice at  $0^{\circ}$  with a kilogram of water at  $79^{\circ}$ . The mean between  $0^{\circ}$  and  $79^{\circ}$  is  $39.5^{\circ}$ , which would have been the temperature obtained by mixing a kilogram of *water* at  $0^{\circ}$  with an equal weight at  $79^{\circ}$ . In the case, however, where ice is used the temperature of the two kilograms is found to be  $0^{\circ}$ , so that in converting the solid ice into liquid water, as much heat has been absorbed as would have raised two kilograms of water  $39.5^{\circ}$ , or one kilogram  $79^{\circ}$ . The same amount of heat which is rendered *latent* during the passage of ice into water is rendered again *sensible* on the return of water into ice. In the same way that heat is absorbed during the passage of matter from the solid to the liquid condition, so heat is further absorbed during the passage of the liquid to the gaseous. If a flask of cold water be placed over a source of heat it will be found that the temperature rises steadily for each increment of heat until the boiling point is reached, when steam is given off, and any increased heat applied to the flask has no effect in raising the temperature to a higher degree, but simply that of increasing the rate of ebullition. The excess of heat is here being used to convert the water into the gaseous condition, and a corresponding degree of heat is evolved, or rendered sensible, during the return of steam to the liquid form of water. This may be roughly demonstrated as follows:—If 2 kilograms of water at  $0^{\circ}$  are raised to  $100^{\circ}$  by the admission of steam at  $100^{\circ}$ , the whole is

found to weigh 2·374 kilograms, and, therefore, it must be assumed that ·374 kilograms of steam at  $100^{\circ}$  have, in condensing to the liquid form, raised 2 kilograms of water from  $0^{\circ}$  to  $100^{\circ}$ , and 1 kilogram of steam at  $100^{\circ}$  would, therefore, raise 5·36 kilograms of water at  $0^{\circ}$  through  $100^{\circ}$ , or 536 kilograms through  $1^{\circ}$ . The *latent heat* of steam is said therefore to be *536 thermal units*. At whatever temperature a liquid evaporates, whether rapidly at its boiling point, or slowly and almost insensibly at much lower temperatures, a proportionate degree of heat is always rendered latent. This has been already proved in the case of water, but admits of corroborative experiments. If a little ether or other volatile liquid be placed upon the hand, and the breath directed on the part to promote evaporation, the abstraction of heat will be very sensibly felt. In a beautiful apparatus contrived by Dr Wollaston, termed a Cryophorus, water is absolutely frozen by the rapid evaporation of its own vapour. The instrument consists of a bent tube having a bulb at each end. The tube is exhausted of air, one of its bulbs containing a little water. When the bulb not containing water is immersed in a freezing mixture, the aqueous vapour which it contains is condensed, and evaporation sets in from the water in the other bulb to supply the place of that which has been removed, and the condensation and consequent evaporation proceeds so rapidly that the water is speedily frozen. All machines for the artificial production of ice are dependent in their action on the abstraction of heat by the evaporation of a liquid. Various liquids have been used for the purpose, the principle ones being water, ammonia, ether, sulphurous acid, and carbon disulphide. In cold producing machines, the rapid evaporation is produced in the freezing vessel by exhaustion of the vapour of the liquid used, by means of a powerful pump, and the pump is so constructed as to exhaust on the one side, and compress on the other. The compression, assisted by the condensa-

ing arrangement round which cold water circulates, reduces the vapour which is removed from the freezing vessel to the liquid form again, and it can then be used for the production of a fresh quantity of ice.

Water, as well as most other liquids, evaporates with greater or lesser rapidity at all temperatures. If, for instance, a few drops of water are introduced into the upper part of a barometer, the level of the mercury is immediately depressed, and such depression increases with increase of temperature, until at  $100^{\circ}$  the mercury in the tube has sunk to the level of that outside. It will be understood, therefore, that at  $100^{\circ}$  the pressure of aqueous vapour is equal to that of the atmosphere. This pressure exerted by the vapour of water is termed *elastic force*, or more generally *vapour tension*, and it will be seen that *the boiling point of a liquid is that temperature at which the tension of its vapour is equal to that of the pressure of the superincumbent atmosphere*. Thus the boiling point of water is found to vary with the height of the barometer, and at elevated places such as mountains, where the atmospheric pressure is considerably less than at the level of the sea, the boiling point of water is much lower than  $100^{\circ}$ . Water is taken as the standard in taking the specific gravity of liquids, as hydrogen is taken as the



Fig. 4.

standard for gases. The term specific gravity, as applied to liquids, means the weight of a certain volume of the liquid, as compared with an equal volume of water at the same temperature. Specific gravities are taken in a *small bottle*, similar in shape to that shown in Fig. 4.

Assuming that this bottle holds, when filled up to the mark in the neck, exactly 1000 grams of distilled water at its maximum density, viz., 4°, then when filled with a different liquid, the weight of the same fluid bulk at the same temperature will vary in proportion; in the case of the strongest solution of ammonia it will be 880 grams, of pure sulphuric acid 1854 grams, and so on. Taking the 1000 grams of water as the unit and calling it 1, the specific gravity of the liquid ammonia will be .880, and that of sulphuric acid 1.854.

Water does not occur in nature in the perfectly pure state, that collected from springs, rivers, and lakes always containing various substances in solution derived from the strata through which it has passed, whilst sea water contains large quantities of sodium chloride, besides smaller proportions of other salts. Rain water, which is the purest form in which natural water can be obtained, contains dissolved gases, and that collected in the neighbourhood of large cities contains various other additional impurities, chiefly of an organic nature.

The substances occurring in solution in ordinary water are the carbonates and sulphates of lime and magnesia, chloride of sodium, and small quantities of silica, alumina, and alkaline salts, with occasionally a little of the chlorides of calcium and magnesium. A *soft* water has very little solid matter in solution; while in a *hard* water the amount of dissolved salts is, as a rule, considerably greater. The hardness of water is of two kinds—*permanent*, when the water contains the sulphates of lime or magnesia, or both salts together; and *temporary*, when the greater amount of the lime and magnesia is present as carbonate, in which case the water may be softened by simple boiling. The capability of softening such water by boiling arises from the fact that the carbonates of lime and magnesia, although insoluble in perfectly pure water, are dissolved by water holding free carbonic acid in solution,



which is the case in most natural waters. By the application of heat, the carbonic acid is expelled, and the carbonates of lime and magnesia become insoluble, and are precipitated. Natural waters may contain a very varying quantity of substances in solution, and may be conveniently classified according to the amount and character of such dissolved constituents. Thus, water which contains much lime, more especially in the form of calcium carbonate, is said to be *calcareous*; when sufficient mineral salts are present to impart a distinct taste, the water is termed *mineral*, or *saline*; when iron is present, the term *chalybeate* is used; *effervescent*, when freely evolving gases; and *sulphurous*, when containing sulphuretted hydrogen, or sulphurous acid.

#### EXAMINATION OF WATERS FOR DOMESTIC PURPOSES

WATERS required for domestic purposes should be free from organic matters, more especially those of animal origin, and should not contain suspended matter, or an undue quantity of salts in solution. Waters moderately charged with lime and magnesia salts have not been proved directly injurious to health, but they are not adapted for washing purposes, as the lime and magnesia form insoluble compounds with the fatty acids of the soaps, and so prevent "lathering."

The examination of a water, in order to ascertain whether it is suitable for domestic purposes, is generally confined to the following particulars:—

- Total solid matter
- Chlorine
- Ammonia
- Organic matter
- Nitrogen, present as nitrates and nitrites
- Hardness

**TOTAL SOLID MATTER** is determined by evaporating a measured quantity of the water at a steam heat in a

platinum basin, drying in the air-bath at from 100° to 120°, and finally ascertaining the weight of the residue.

CHLORINE is generally determined volumetrically by the use of a standard solution\* of silver nitrate. The use of the chlorine determination is mainly as a help in the detection of sewage contamination. Urine contains considerable quantities of chlorine, as sodium chloride, which, as a necessary consequence, finds its way into the sewage; and any infiltration of sewage into a naturally pure water thus gives rise to an increased amount of chlorine. At the same time, a water may naturally contain a comparatively large amount of chloride, derived either from a peculiarity in the composition of the strata through which it has passed, or in consequence of its being drawn from a source in proximity to the sea or to a tidal river. The presence, therefore, of a comparatively large amount of chlorides is only suspicious where associated with other evidences of contamination.

AMMONIA.—The ammonia existing in naturally pure waters is, as a rule, exceedingly small. When a water is found to contain an appreciable quantity of this substance, it is generally derived from animal contamination, and the estimation of the ammonia in a water is, therefore, of importance. When nitrogenous organic substances decay, the nitrogen which they contain assumes the form of ammonia, which, however, may become subsequently oxidised to the form of nitrates and nitrites by filtration through a porous soil. The presence of ammonia conjointly with organic matter is thus taken as an evidence of *recent* or existing contamination, while the presence of nitrates and nitrites are only indicative of past, and consequently harmless, pollution. Advantage is taken of

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\* The term "standard solution" is used to express the fact that the liquid contains a known quantity of some re-agent in every volume measure.

the volatile character of ammonia in estimating its quantity in waters. The water is subjected to distillation, and the whole of the ammonia present is then found in the first portions of the distillate. The actual estimation is effected by means of a re-agent, known as Nessler-test, which consists of a saturated solution of iodide of mercury in iodide of potassium, rendered alkaline by the addition of caustic soda. This re-agent gives a brown coloration, with exceedingly small quantities of ammonia, the intensity of such coloration being in strict proportion to the quantity of ammonia present.

The distillate is placed in a cylindrical glass vessel resting on a white porcelain slab, and a measured quantity of Nessler-test added, when a brown coloration is produced in the event of ammonia being present. A second vessel of the same dimensions as the first is then placed on the porcelain slab by the side of the other, and some distilled water free from ammonia poured in. Dilute standard solution of ammonia is then added in such quantity as is judged to correspond to the quantity of ammonia in the distillate, and, finally, Nessler-test added in the same quantity as before. The degree of coloration is then noticed, and compared with that produced in the distillate; and if the intensity of the two tints does not correspond, a further trial is made, until an exact correspondence of colour is obtained. It will be obvious that the quantity of ammonia which is contained in the amount of standard solution used in the comparison, represents the quantity of ammonia present in the distillate.

**ORGANIC MATTER.**—A rough test for the presence of organic matter in any sample of water is the addition of a dilute solution of potassium permanganate in just sufficient quantity to impart a delicate but distinct pink colour. If the sample be pure, the colour will remain unimpaired for some considerable time; but in the event of organic impurity being present, the colour

fades more or less rapidly. The objection to this test is that the colour of the permanganate is destroyed by nitrites and by ferrous salts, as well as by organic matter; and a further objection is also that no distinction can be drawn between a water contaminated by simple vegetable matter—such, for instance, as peat—and one in which the contamination is of sewage origin, and may, therefore, be much more injurious. The presence of organic matter in water may be recognised by heating the residue obtained on evaporation to redness, when a blackening occurs from the charring of the organic matter; and if, at the same time, an odour be evolved which resembles burnt feathers, such organic matter is of animal origin.

For the systematic examination of waters in order to discover organic contamination, and to gain information as to the amount of such contamination, two methods are in use among chemists, termed respectively Wanklyn and Chapman's, and Frankland's, from the names of their respective inventors. In both of these methods the nitrogen is taken as the principal measure of the amount of contamination, as harmless organic substances, such as decayed vegetable matter, contain very little nitrogen. Wanklyn and Chapman's process consists in distilling the water in a retort, firstly, by itself, to get any ammonia which may be present, and, subsequently, with an alkaline solution of potassium permanganate. By the action of the alkaline permanganate, any organic matter which is present in the water is decomposed, the nitrogen which it contains being evolved as ammonia, which passes over in the distillate, and can then be estimated by Nessler-test. The whole of the nitrogen present is never obtained, but a comparatively fixed percentage appears to be given off, so that the results become strictly comparative, and a pure water may be thus compared with one that is contaminated.

Frankland's process is in reality a modification of

organic analysis (see Chapter on Organic Chemistry). The water residue is burnt in a combustion tube with oxide of copper, when the nitrogen of the organic matter is given off in the gaseous state, while the carbon is evolved as carbonic acid, the gases being collected and their volume measured. As the volume of gas obtained is, as a rule, exceedingly small, the whole operation requires the greatest skill and care. The advantages of Frankland's method are twofold. In the first place, the *whole* of the nitrogen present is obtained and estimated; and, in the second place, as the carbon is also obtained, the relation between the two substances, carbon and nitrogen, indicates the *character* of the organic matter present. In organic matter of *animal* origin, the amount of nitrogen is large in proportion to the carbon, whilst in vegetable matter the reverse is generally the case.

NITROGEN PRESENT AS NITRATES AND NITRITES.—The value of estimating the amount of these substances present in a water is that they are generally considered as evidences of animal contamination. Neither nitrates nor nitrites are in themselves hurtful, but their presence proves that some channel of communication either exists or has existed between the place from which the water is derived and some contaminating source. One exception must, however, here be made in favour of chalk waters, which are of exceptional purity, and yet frequently contain a somewhat large amount of nitrates. The estimation of nitrates and nitrites may be conveniently effected by acting on a measured quantity of the water, which has previously been rendered strongly alkaline by the addition of caustic soda, by metallic aluminum in thin sheet or foil. The nitrogen of the nitrates and nitrites then assumes the form of ammonia, which is estimated by Nessler in the usual way.

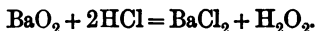
**HARDNESS.**—The estimation of the amount of hardness in a water is principally of use in determining the

fitness of such water for washing purposes. For this purpose a process devised by Dr Clarke, and hence called Clarke's process, is used. A measured quantity of the water is introduced into a small stoppered bottle, and a solution of soap of known strength added by degrees from a graduated tube. After each addition of the soap solution the bottle is briskly shaken, and as long as salts of lime or magnesia are present in solution, a combination occurs between these substances and the fatty acids of the soap, a white, curdy precipitate being formed. Directly, however, all the lime and magnesia is precipitated, and there is consequently *free* soap present in the solution, a lather is formed on shaking, and the formation of this lather is taken as representing the termination of the experiment. The number of measures of soap solution used is then noted, and the water is accordingly stated to be of so many degrees of hardness. The *permanent* hardness is obtained by boiling a measured quantity of the water for a period of one hour, which causes the precipitation of the carbonates of lime and magnesia, after which the water is allowed to cool, diluted to its original volume with distilled water, and the degree of hardness estimated in the manner already described. The *temporary* hardness is obviously the difference between the *total* or original and the *permanent*.

When a water is hard from the presence of the carbonates of lime and magnesia, it admits of being softened by a very simple process. Instead of expelling by boiling the carbonic acid which retains the lime and magnesia salts in solution, the carbonic acid may be removed by the addition of a solution of lime. Carbonate of lime is thus formed, which precipitates, and the carbonates of lime and magnesia previously held in solution by the excess of carbonic acid are also thrown down. This method, known as Clarke's process, is now carried out in *many places* on a considerable scale.

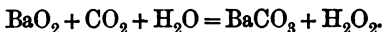
*HYDROGEN DIOXIDE,  $H_2O_2$ ,—Hydroxyl,—*may be pre-

pared from barium dioxide by the action of hydrochloric acid—



By this method a mixture of hydrogen dioxide and barium chloride is obtained, and it requires a somewhat elaborate process to entirely remove the barium chloride.

A purer product may be obtained by suspending barium dioxide in water and passing a current of carbonic acid gas, when barium carbonate is produced together with hydrogen dioxide.



The barium carbonate being insoluble, settles down as a white precipitate, leaving a clear aqueous solution of hydrogen dioxide. This solution may have the greater part of its water removed by evaporation in the exhausted receiver of an air-pump. All the water cannot, however, be eliminated. The fluid thus obtained has a specific gravity of 1.45. It is a colourless, syrupy liquid, very prone to decomposition. The slightest elevation of temperature causes the evolution of oxygen, and at 100° the gas is evolved very rapidly. Hydrogen dioxide possesses powerful oxidising properties, rapidly bleaching and destroying vegetable colouring matters, and converting some of the sulphides into sulphates.

## NITROGEN

SYMBOL, N

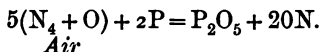
COMBINING WEIGHT, 14

The name nitrogen signifies generator of nitre. Nitrogen is sometimes called azote ( $\alpha$ , privative, and  $\zeta\omega\eta$ , life).

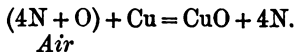
Discovered by Rutherford in 1772, and subsequently identified by Lavoisier as a constituent of the atmosphere.

**DISTRIBUTION.**—Nitrogen occurs in the free state in the atmosphere, of which it constitutes four-fifths by volume. In combination, it occurs largely in the vegetable, animal, and mineral kingdoms. It is a constituent of many products of plant life, forms a considerable part of the muscular tissue of animals, and in the mineral kingdom occurs in the nitrates of sodium and potassium, and in coal.

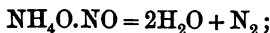
**PREPARATION.**—Nitrogen is most easily prepared from atmospheric air by the abstraction of oxygen. By placing a fragment of ignited phosphorus under a bell-glass containing air, and standing over water, the phosphorus continues to burn until the oxygen has entirely disappeared. Phosphorus pentoxide is formed in white flakes.



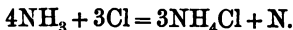
Nitrogen may also be prepared by heating muscular fibre, or other similar nitrogenous organic substance, with dilute nitric acid, and also by passing atmospheric air over metallic iron or copper at a red heat: oxygen is absorbed, the metal is converted into oxide, and the nitrogen passes on unchanged.



Nitrogen may also be prepared by the action of heat on ammonium nitrite, thus:—



and, further, by passing chlorine gas through a solution of ammonia, taking care to keep the ammonia in excess,



**PROPERTIES.**—Nitrogen is a colourless, invisible gas, possessing neither taste nor smell. It is slightly lighter than air, and does not support either combustion or animal life, although entirely non-poisonous. In its



free condition nitrogen is characterised by its singularly inactive properties, most of its compounds with the other elements being formed by indirect means. Although so inactive in itself, it forms many compounds which possess strikingly active properties, prominently among which may be mentioned nitric acid and ammonia—the first compound being a powerful acid, and the latter a powerful base.

Nitrogen is very slightly soluble in water, 100 measures at a temperature of  $15^{\circ}$  dissolving only 1.5 volume of the gas. As already mentioned, nitrogen constitutes about four-fifths of the atmosphere, its function being simply that of a diluent in moderating the active properties of the oxygen with which it is mixed, and thus rendering it suitable to the ordinary conditions of existence. That the atmosphere consists of a simple *mechanical mixture* of oxygen and nitrogen may be proved in several ways. When air is agitated with pure distilled water, the amounts of oxygen and nitrogen dissolved by the water are simply proportionate to the comparative solubilities of the two gases, and bear no relation to their atomic weights, thus proving the mechanical nature of the gaseous mixture. Again, the density of air is the same as that of a mixture of the two constituent gases in the proper proportions, and such a mixture exhibits all the physical and chemical properties of atmospheric air.

The composition of the atmosphere, freed from all contaminating substances, and thoroughly dried, is as follows :—

	By volume	By weight
Nitrogen . . .	79.1	76.9
Oxygen . . .	20.9	23.1
	<hr/> 100.0	<hr/> 100.0

The atmosphere is not, however, a simple mixture of nitrogen and oxygen, but is always more or less charged *with aqueous vapour*, and contains, besides, a small

quantity of carbonic acid and other impurities. The average composition is as follows:—

Nitrogen	.	.	.	.	.	77.95
Oxygen	.	.	.	.	.	20.61
Aqueous vapour (variable)	.	.	.	.	.	1.40
Carbonic anhydride	.	.	.	.	.	0.04
Nitric acid	}	.	.	.	.	traces
Ammonia						
Marsh gas						
Sulphuretted hydrogen	}	near towns .				traces
Sulphurous anhydride						
						100.00

The composition of air may be proved—

1. By introducing a known volume into a graduated glass tube, and absorbing the oxygen by means of an alkaline solution of potassium pyrogallate, when the residual gas will be found to exhibit all the neutral properties of nitrogen, and to measure four-fifths of the original volume. Fig. 5 shows an ordinary graduated glass tube employed in the experiment.

2. By passing a known volume of dry air over heated metallic copper, when the increase which the metal suffers in weight will give the amount of oxygen present.

3. By means of the Eudiometer. A measured volume of air, previously saturated with aqueous vapour, is mixed with an excess of pure hydrogen, and the total volume noted. The mixture is then exploded by passing an electric spark. As one volume of oxygen unites with two volumes of hydrogen to form water, it follows that one-third of the total contraction represents the amount of oxygen present. The amount of nitrogen is obviously the difference

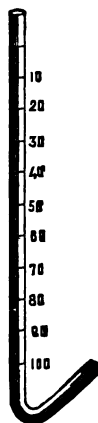


Fig. 5.

between the volume of oxygen found and the volume of air originally taken.

The amount of moisture and of carbonic anhydride contained in the air may be determined by the following method. A known volume of air is passed through—

- (a.) A tube charged with fused calcium chloride broken into small pieces.
- (b.) A bulb tube containing solution of potash.
- (c.) A further tube containing fused calcium chloride.

The weight of tube *a* is carefully ascertained before making an experiment, and tubes *b* and *c* also carefully weighed together. Tube *a* absorbs aqueous vapour from the air, and the increase in weight, therefore, represents the amount of this substance present; while tube *b* absorbs the carbonic anhydride, tube *c* arresting any water vapour which the air takes up from the potash solution.

Carbonic acid may likewise be determined by passing a known volume of the air with a measured quantity of a solution of barium hydrate, the strength of which has been previously ascertained by means of a standard solution of oxalic acid. The barium hydrate unites with the carbonic anhydride to form insoluble barium carbonate, the alkalinity of the solution becomes thereby proportionately less. By filtering the solution from the suspended barium carbonate, and ascertaining the strength of the filtrate by means of standard oxalic acid, the loss of alkalinity may be ascertained, and the equivalent of carbonic anhydride found.

ORGANIC IMPURITIES may be detected in air by passing it through a dilute solution of potassium manganate, which will become more or less quickly decolorised according to the amount of organic matter present.

*Ammonia* may be detected and estimated in air

drawing a volume of the air through some pure distilled water, and subsequently estimating the ammonia by means of Nessler-test. (See Chapter on WATER ANALYSES.)

The presence of sulphuretted hydrogen may be ascertained by the use of paper moistened with a solution of acetate of lead, which becomes discoloured by this impurity.

Sulphurous acid may be detected by the use of paper moistened with a solution of potassium iodate and starch. Paper so prepared becomes blued by the action of sulphurous acid, but it is also affected by ozone and by nitrous acid.

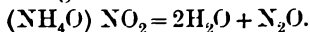
**PRINCIPAL COMPOUNDS OF NITROGEN.**—Chief among the compounds of nitrogen are its oxides, which are five in number, as follow :—

Nitrous oxide, or nitrogen monoxide .	$N_2O$
Nitric oxide, or nitrogen dioxide .	$NO$
Nitrous anhydride, or nitrogen tri- oxide . . . . .	$N_2O_3$
Nitric peroxide, or nitrogen tetroxide	$NO_2$
Nitric anhydride, or nitrogen pent- oxide . . . . .	$N_2O_5$

The compounds  $N_2O_3$  and  $N_2O_5$  are the anhydrides of the acids  $HNO_2$  (nitrous acid), and  $HNO_3$  (nitric acid).

The term anhydride is often applied to compounds which form acids by union with water, and derived from *α*, privative, and *ὕδωρ*, water.

NITROUS OXIDE,  $N_2O$ , is also sometimes called "laughing gas," from the peculiarly exhilarating effects which it often produces when breathed by man. The gas is best prepared by exposing ammonium nitrate to a heat not exceeding  $250^\circ$  in a flask or retort.



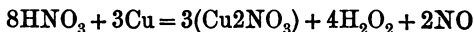
The gas should be collected over warm water, and

when required for respiration, care should be taken that it is pure.

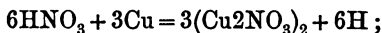
At ordinary temperatures, nitrous oxide is a colourless gas, having a faint agreeable odour, and sweet taste. It supports combustion, but may be distinguished from oxygen by its greater solubility in water, 100 parts of which at 0° dissolve 130 volumes of the gas. A remarkable feature of nitrous oxide is that when carbon is burnt in it with the formation of CO, 40,400 more units of heat are evolved than when the carbon is consumed in oxygen. This fact is contrary to the usual law that heat disappears during decomposition.

Nitrous oxide may be condensed by pressure to a colourless, mobile liquid, which may be frozen to a snowy white solid by exposure to the cold produced by a bath of ether and solid carbonic anhydride.

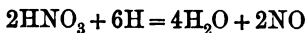
NITRIC OXIDE, NO, (sometimes written N<sub>2</sub>O<sub>2</sub>) is best produced by the action of nitric acid diluted with about twice its bulk of water upon clippings or boring of copper.



The action may be regarded as taking place in two stages, in the first of which cupric nitrate is formed with liberation of hydrogen.



while in the second stage the six equivalents of nascent hydrogen decompose two equivalents of nitric acid, thus—



The reaction may be facilitated by the application of gentle heat, but the lower the temperature employed the purer is the resulting product. Other metals such as lead, silver or bismuth, may be substituted for the copper, but a stronger acid or higher temperature is required. Nitric oxide is a colourless gas

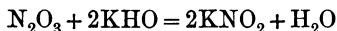
Parent gas very sparingly soluble in water. It may be distinguished from all other gases by the production of deep orange red fumes when it is mixed with oxygen. Nitric oxide is absorbed by ferrous salts forming a deep brown, almost black liquid, and it is likewise absorbed by chromous, stannous, and mercurous salts. It enters also into several compounds as a monatomic radical called nitrosyl, or nitroxyl, one equivalent of which replaces one atom of hydrogen in combination.

NITROUS ANHYDRIDE,  $N_2O_3$ , is formed together with nitric peroxide when nitric oxide is brought in contact with oxygen. It may be obtained in a pure condition by exposing to an exceedingly low temperature a mixture of two volumes of nitrous oxide and one volume of oxygen; nitrous anhydride then condenses as a blue liquid which emits red fumes, and which is decomposed by water with the formation of nitric acid and nitric oxide.



Liquid nitrous anhydride may also be prepared by heating one part of starch with eight parts of nitric acid of specific gravity 1.25, and passing the evolved gas through a tube containing fused calcium chloride to absorb moisture, and finally into a bulb tube cooled to  $93.6^\circ$ .

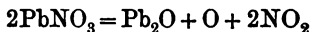
Nitrous acid appears to be formed when a small quantity of ice cold water is added to liquid nitrous anhydride, but the least elevation of temperature leads to decomposition. Nitrites are, however, a well defined series of salts. They are, as a rule, soluble in water. Nitrites of the alkalis may be formed by passing gaseous nitrous anhydride into a solution of the alkaline hydrate, thus—



The above shows the formation of potassium nitrite by this means.

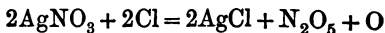
*NITRIC PEROXIDE*,  $NO_2$ , (sometimes written  $N_2O_4$ ) is

the principal product of the action of excess of oxygen on nitric oxide at ordinary temperatures. It is, however, best prepared by heating well dried lead nitrate in a hard glass retort. Oxygen and nitric peroxide are evolved, the latter of which may be condensed by the action of a freezing mixture.



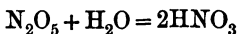
Nitric peroxide at very low temperatures is a transparent crystalline solid, which, by a slight elevation of temperature, forms a colourless liquid, which, on a further increase of heat, is coloured yellow or orange, and eventually becomes at the ordinary temperature a gas of a deep brownish-red colour and suffocating odour. This gas is decomposed by water and by metallic oxides and hydrates, forming mixtures of nitrates and nitrites.

NITRIC ANHYDRIDE,  $\text{N}_2\text{O}_5$ , (sometimes called anhydrous nitric acid) is prepared by passing perfectly dry chlorine gas over dried silver nitrate heated to  $95^\circ$ , silver chloride is then formed, and nitric anhydride and oxygen given off.



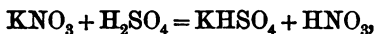
The nitric anhydride must be condensed by means of a freezing mixture. This compound may also be prepared by adding phosphorous pentoxide to pure nitric acid. In its pure state it is a white crystalline substance, melting at  $30^\circ$  and boiling at  $45^\circ$ . It is of unstable character.

NITRIC ACID,  $\text{HNO}_3$ , may be formed by the union of one equivalent of nitrogen pentoxide with one equivalent of water.



Nitric acid may be more conveniently prepared by heating potassium or sodium nitrate with strong sulphuric acid in a hard glass retort.

is customary to employ a larger proportion of nitric acid, when a lower temperature may be used. Single equivalents of potassium nitrate and sulphuric acid are used, the reaction is as follows:—



When acid potassium sulphate is formed in place of neutral salt.

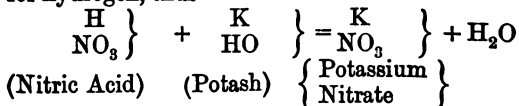
Large scale nitric acid is prepared by heating potassium nitrate and sulphuric acid in iron cylinders, the operation being effected in a series of stoneware vessels or bottles. Sodium nitrate is advantageously substituted for potassium nitrate in the preparation of nitric acid on a large scale, for two reasons, firstly, on account of its lower price; and secondly, by reason of obtaining a larger yield of acid, as will be seen at once from a comparison of the respective equivalents. The equivalent of potassium nitrate being 101.2, that of sodium nitrate 85; producing in each case a monovalent, or 63 parts of liquid nitric acid, it is evident that, taking equal weights of each salt, the amount of acid from the latter is considerably greater than from the former.

Nitric acid is a colourless, strongly-fuming liquid of specific gravity 1.5. It has not a constant



a very dilute acid is first obtained. The result in both cases is that the acid of the composition named is prepared after the distillation has proceeded some little time. The strength of the acid, which distils at the fixed boiling point of 120·5, however, varies slightly with the fluctuations of atmospheric pressure.

Nitric acid, especially when heated, is a very powerful oxidising agent. It contains 75 per cent. of oxygen, a large portion of which is readily given up to any substances capable of oxidation. This property is well illustrated by its action upon such metals as lead, copper, or silver, all of which are quickly oxidised and dissolved by even dilute nitric acid with evolutions of red fumes of nitric peroxide. Many of the non-metallic elements, such as phosphorus, sulphur, iodine, etc., are also immediately and violently oxidised by the action of nitric acid in its concentrated state. It also exercises a peculiar action on many organic substances, forming well defined compounds, which will receive attention under "Organic Chemistry." Free nitric acid stains the skin, and many other nitrogenous organic substances of a yellow colour, which is intensified by the action of ammonia. Nitric acid forms an extensive and important series of salts termed nitrates, which are nearly all soluble in water, and many of which are largely employed in the arts and manufactures; it is monobasic, that is to say, it contains one atom of replaceable hydrogen. When a nitrate is formed by the union of nitric acid with a metallic base, the action which occurs may be conveniently regarded as a substitution of metal for hydrogen, thus—



This view of the formation of salts has led to the modern definition of an *acid* as "a compound containing hydrogen, the whole or part of which is displaceable

metal," and of a *salt* as "a compound derived from an acid by the displacement of a part or the whole of its hydrogen by a metal."

A nitrate may be identified by its evolving red fumes when heated in a test tube with strong sulphuric acid and copper turnings. Soluble nitrates treated with stannous acid decolorise a solution of indigo, a result due to oxidation; they also produce a dark coloured compound with ferrous sulphate. The last named test is applied by mixing the solution to be examined with an equal volume of strong sulphuric acid in a test tube, and after the mixture has cooled, pouring upon the surface of the liquid, a saturated solution of the salt, when if a nitrate is present, a dark brown ring is formed at the juncture of the two liquids. The presence of nitrates in natural waters, and their detection and estimation has been already noticed.

The following table is an abridgment of the characteristics of the oxides of nitrogen:—

[TABLE

*Table showing the leading Characteristics of the Oxides and Oxacids of Nitrogen :—*

NAME	FORMULA	LEADING CHARACTERISTICS
Nitrogen Monoxide	$N_2O$	Colourless inodorous gas, of sweet taste, liquifiable by great pressure or extreme cold; slightly soluble in cold water; supports combustion, and exerts an intoxicating effect on the human frame.
Nitrogen Dioxide	$N_2O_2$ or $NO$	Colourless gas, forming red fumes with oxygen.
Nitrogen Trioxide	$N_2O_3$	Red fuming gas, condensing at $18^\circ$ to a volatile blue liquid.
Nitrogen Tetraoxide	$N_2O_4$ or $NO_2$	Deep brownish red gas, of suffocating odour. Soluble in water; converts metallic hydrates into a mixture of nitrate and nitrite.
Nitrogen Pentoxide	$N_2O_5$	Unstable white solid substance, melting at $30^\circ$ and boiling at $45^\circ$ ; forms nitric acid with water.
Nitric Acid	$HNO_3$	Colourless fuming liquid, of specific gravity 1.51, possessing powerful oxidising properties. Stains the skin yellow, and forms nitrates with bases.
Nitrous Acid	$HNO_2$	Unstable liquid which rapidly undergoes decomposition; forms nitrites with bases.

All the oxides of nitrogen, as also free nitrogen itself, may be prepared directly or indirectly from nitric acid, and as this acid can be procured from potassium nitrate, both nitrogen and its oxides are thus obtainable (indirectly) from this salt. A table showing the method by which nitrogen and its oxides may be prepared from nitric acid is appended.

[TABLE

*Table showing the Mode of Preparing Nitrogen and its Oxides from Nitric Acid (HNO<sub>3</sub>):—*

NAME	FORMULA	PREPARATION
Nitrogen	N	By heating muscle or similar substances with the dilute acid.
Nitrogen Monoxide or Nitrous Oxide	N <sub>2</sub> O	By neutralising the acid with ammonia, evaporating the solution, and heating the solid ammonium nitrate. $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$
Nitrogen Dioxide or Nitric Oxide	N <sub>2</sub> O <sub>2</sub> or NO	By heating the acid with copper turnings. $3\text{Cu} + 8\text{HNO}_3 = 3(\text{Cu}2\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
Nitrogen Trioxide or Nitrous Anhydride	N <sub>2</sub> O <sub>3</sub>	By mixing four volumes of dry nitrogen dioxide obtained as above with one volume of oxygen and cooling to 18°. $2\text{NO} + \text{O} = \text{N}_2\text{O}_3$
Nitrogen Tetroxide	N <sub>2</sub> O <sub>4</sub> or NO <sub>2</sub>	By neutralising the acid with lead, evaporating solution to dryness, and heating the solid lead nitrate. $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
Nitrogen Pentoxide or Nitric Anhydride	N <sub>2</sub> O <sub>5</sub>	By neutralising the acid with silver, evaporating to dryness, and heating the dry silver nitrate in a current of chlorine. $2\text{AgNO}_3 + 2\text{Cl} = 2\text{AgCl} + \text{N}_2\text{O}_5 + \text{O}$

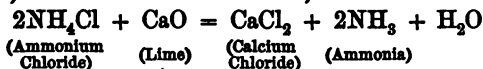
## NITROGEN AND HYDROGEN

AMMONIA— $\text{NH}_3$ 

Nitrogen and hydrogen cannot be made to unite directly with each other, but their union occurs during the decomposition of nitrogenous animal, and vegetable matters, either slowly at ordinary temperatures or more rapidly by the action of heat. The ammonia arising from the decay of organic matters containing nitrogen passes into the air and the soil, and plays an important part in the growth of plants which obtain their nitrogen almost entirely in the form of ammonia.

AMMONIA derives its name from its being first prepared by the Arabs near the temple of Jupiter Ammon by heating camels' dung. It is often called the volatile alkali, and sometimes "spirits of hartshorn," a term derived from the fact of its preparation by the old alchemists by distilling stags' horns in closed vessels. Guano, the dried and decomposed excrements of sea-birds, owes its chief manurial value to the large amount of ammonia which it contains.

PREPARATION.—Ammonia is best prepared by acting upon one of its salts with a fixed alkali or alkaline earth, with the assistance of heat, thus—



The materials are intimately mixed in a finely powdered condition, and placed in a Florence flask provided with a glass tube for conveying the gas into a receiver. The ammonia comes off as a gas on the application of heat, and as it is very soluble in water must be collected over mercury or by displacement. When nitrogenous organic matter, such as bones, animal refuse, and coal, are subjected to a red heat in closed vessels, the greater part of the nitrogen present is evolved in the form of ammonia, partly free, and partly as carbonate and other salts. The ammoniacal liquid occurring as

a bye product in the destructive distillation of coal for the manufacture of gas is the source of nearly the whole of the ammonia salts of commerce.

**PROPERTIES.**—Ammonia is a colourless gas, possessing a most pungent and characteristic odour. It is alkaline in its properties, restoring the blue colour to reddened litmus paper, and neutralising acids to form salts. Ammonia is liquified by exposure to a pressure of about seven atmospheres. The gas is very soluble in water. At the ordinary temperature and pressure, water will dissolve about 600 times its volume; while at  $0^{\circ}$  no less than 1050 times its volume is dissolved. The strongest ammonia solution of commerce has a specific gravity of 880, and contains 27.3 per cent. of  $\text{NH}_3$ . Ammonia gas is decomposed by the passage of a series of electric sparks, its volume becoming doubled, and the gaseous mixture obtained consisting of hydrogen and nitrogen in the proportion of three volumes of the former to one of the latter. Ammonia much resembles the fixed alkalis—potash and soda—in its properties, and, like them, unites with acids to form a large class of soluble salts. These salts will be described under “Ammonium” in connection with those of potassium and sodium.

## NITROGEN AND CHLORINE

**NITROGEN CHLORIDE** is a remarkable compound formed when excess of chlorine is brought in contact with a solution of ammonia. It is an oily liquid, in which the attraction between the constituent elements is so slight, that even the slightest touch is sufficient to cause the compound to explode with the greatest violence. The composition of nitrogen chloride has not been definitely determined, but it is considered to be either  $\text{NCl}_3$ , or  $\text{NCl}_3\text{NHCl}_2$ .

Appended is a table showing the preparation and properties of the three previously described elementary gases—oxygen, hydrogen, and nitrogen :—

## Oxygen, Hydrogen, and Nitrogen :—

NAME	SYMBOL	METHOD OF PREPARATION	PROPERTIES
Oxygen	O	By heating mercuric oxide— $\text{HgO} = \text{Hg} + \text{O}$ By the action of heat on manganese dioxide— $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ By heating potassium chlorate— $\text{KClO}_3 = \text{KCl} + \text{O}_3$	Great supporter of combustion and animal life. Combines with all the elements, except fluorine, to form compounds called oxides. This union or <i>oxidation</i> is frequently attended with evolution of heat and light.
Hydrogen	H	By displacement from its acid compounds by a metal such as zinc or iron— $\text{H}_2\text{SO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{H}_2$ $2\text{HCl} + \text{Fe} = \text{FeCl}_2 + \text{H}_2$ also By displacement from water by an alkali metal— $\text{H}_2\text{O} + \text{Na} = \text{NaHO} + \text{H}$	Non-supporter of combustion or of animal life, but itself combustible, burning in air with a blue and intensely hot flame, the sole product of combustion being water. It unites with some of the elements to form <i>hydrides</i> .
Nitrogen	N	From atmospheric air by withdrawal of oxygen by burning phosphorus over water. By passing air over red hot copper— $\text{Cu} + 4\text{N} + \text{O} = \text{CuO} + 4\text{N}$ By heating ammonium nitrite— $\text{NONH}_3\text{O} = \text{N}_2 + 2\text{H}_2\text{O}$	Characterised by its negative properties being neither combustible, nor a supporter of combustion. It does not readily enter into combination, but many of its compounds possess very strongly marked properties.



## CHLORINE

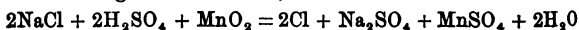
SYMBOL, Cl. COMBINING WEIGHT = 35.5

CHLORINE was discovered by Scheele in 1774, and was named by Sir Humphrey Davy from "*χλωρός*," yellowish green.

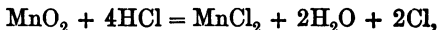
DISTRIBUTION.—Chlorine does not occur in the free state in nature, but is met with plentifully in combination with sodium as rock-salt and sea-salt, and combined with potassium as potassium chloride.

PREPARATION.—Chlorine is generally prepared in one of two ways.

1. By heating a mixture of sodium chloride, manganese dioxide, and sulphuric acid, when free chlorine is evolved, sodium sulphate, manganous sulphate, and water being formed—thus,



2. By subjecting a mixture of manganese dioxide and hydrochloric acid to a gentle heat—



in which manganese dioxide and hydrochloric acid afford manganese chloride, water, and free chlorine. The gas, which is twice as heavy as air, is best collected by displacement as it attacks mercury (mercuric chloride being formed), and is soluble in cold water. The pneumatic trough may, however, be used if charged with warm water, in which chlorine is only soluble to a small degree.

On the basis of the equations given of the action which occurs in the preparation of chlorine by the methods described, calculations may be made of the amounts of the respective materials which must be taken in order to produce any desired quantity of chlorine. Thus, by the first equation, two equivalents of NaCl =  $58.5 \times 2 = 117$ , two of sulphuric acid,  $\text{H}_2\text{SO}_4 = 98 \times 2 = 196$ , and one equivalent of  $\text{MnO}_2 = 107$ , yield two equivalents of chlorine =  $35.5 \times 2 = 71$ . If, therefore, we

desire to find how much of each material must be taken to yield say 100 litres of chlorine, we have, first, converting the volume of chlorine into its corresponding weight = 317.2 grams (11.19 litre = 35.5 grams), to express the sums as follow: First for the quantity of NaCl—

$$71 : 317.2 :: 117 : x$$

$$x = 522.6 \text{ grams NaCl.}$$

Taking the sulphuric acid next—

$$71 : 317.2 :: 196 : x$$

$$x = 877 \text{ grams H}_2\text{SO}_4.$$

Finally, for the amount of manganese—

$$71 : 317.2 :: 107 : x$$

$$x = 478 \text{ MnO}_2.$$

If the chlorine is to be procured from the action of hydrochloric acid on manganese dioxide, then, according to the equation given, one equivalent of  $\text{MnO}_2 = 107$  and four of  $\text{HCl} = 36.5 \times 4 = 146.0$ , yield two equivalents or 71 parts of  $\text{Cl}$ , and the calculation of the amounts of the respective materials necessary for the production of any desired quantity of chlorine can be calculated on these data.

Chlorine is prepared on a large scale by two methods, chiefly for bleaching purposes, and for the manufacture of the so-called chloride of lime. The one is known as Deacon's process, and consists in passing hydrochloric acid gas and air over heated fragments of brick which have been previously soaked in a solution of copper sulphate and dried. The hydrogen of the hydrochloric acid then combines with the oxygen of the air to form water, and free chlorine is evolved. The other method, known as Weldon's process, consists in generating chlorine by the action of manganese dioxide and hydrochloric acid, the chloride of manganese solution formed being treated with lime to precipitate the protoxide of manganese. A current of

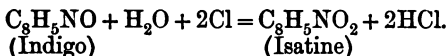
air is then passed through the mixture, which converts the manganese protoxide into the dioxide, which can then be used for the preparation of a fresh quantity of chlorine.

PROPERTIES.—Chlorine is a gas of a peculiar greenish yellow colour, and possessing such a suffocating odour, that the inhalation of an exceedingly small quantity is sufficient to produce violent coughing and irritation. Under a pressure of somewhat less than five atmospheres, it is condensed to a limpid yellow liquid. At a temperature of  $15^{\circ}5$  water dissolves about twice its volume of chlorine, forming a solution possessing the peculiar colour and odour of the gas. Moist chlorine exposed to a cold of  $0^{\circ}$  forms a definite hydrate in yellow crystals ( $\text{Cl}_5\text{H}_2\text{O}$ ). Chlorine has a great affinity for hydrogen, but little affinity for oxygen; it can, however, be made to unite with oxygen by indirect means, and forms a distinct and well-marked series of compounds.

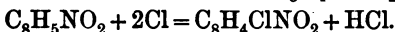
The affinity of chlorine for hydrogen is well illustrated by mixing the two gases together in equal volumes in the dark. If a flame is then applied to the mixture, or if it is even suddenly exposed to direct sunlight, combination ensues with explosion and formation of hydrochloric acid. If a piece of paper be moistened with turpentine, and plunged into a jar of chlorine, the affinity of the chlorine for the hydrogen contained in the oil of turpentine is so great, that combustion at once ensues, hydrochloric acid being formed, and carbon liberated in the free condition as a dense smoke.

The flame of a lighted taper is not extinguished when immersed in chlorine, but diminishes in size, and becomes of a red colour, the hydrogen of the wax uniting with the chlorine to form hydrochloric acid, while the carbon is liberated as a black smoke. The flame of a spirit-lamp becomes luminous when immersed in chlorine, from the liberation of solid carbon per-

ticles. Chlorine acts on many hydrocarbons, often forming compounds in which chlorine is substituted for hydrogen. Thus when marsh gas,  $\text{CH}_4$  (mixed with carbonic acid to moderate the violence of the action), is exposed to daylight, a mixture of chloroform ( $\text{CH}.\text{Cl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) is formed. In some cases chlorine simply unites with a hydrocarbon without removing hydrogen, as in the formation of Dutch liquid  $\text{C}_2\text{H}_4\text{Cl}$  from olefiant gas  $\text{C}_2\text{H}_4$ . The powerful bleaching properties possessed by chlorine is another illustration of its affinity for hydrogen. These properties are only manifested in the presence of moisture, and are due to the breaking up of the water, the hydrogen of which forms hydrochloric acid with the chlorine, while the oxygen is liberated in the nascent condition, a form in which it is peculiarly active in causing oxidation. The bleaching of vegetable colouring matters by chlorine is due to the formation of colourless oxidation products. This may be well illustrated by adding a little chlorine water to such coloured infusions as litmus, turmeric, cochineal, and red cabbage, etc., or to a little solution of indigo, when the colour will in each case be destroyed. In the case of indigo it becomes oxidised to isatine, thus:—



The isatine so formed is then converted by the further action of chlorine into chlorisatine,  $\text{C}_8\text{H}_4\text{ClNO}_2$ , thus:—



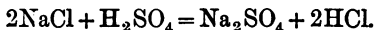
The use of chlorine in commerce for bleaching purposes is very great, principally in cotton, linen, and paper manufactures. It is sometimes used in the gaseous condition, but far more frequently in the form of chloride of lime, the bleaching properties of which are due to the presence of hypochlorous acid. The oxidising powers of chlorine render it of great use as a

disinfectant, and there is probably no agent more powerful for this purpose. Chlorine acts energetically on many of the metals. Powdered antimony or arsenic, or a piece of copper leaf, when immersed in a jar of the gas, spontaneously inflames, and is converted into chloride of the metal. Phosphorus also ignites under the same conditions.

**PRINCIPAL COMPOUNDS.**—Chlorine forms one compound with hydrogen, viz., hydrochloric acid, while with oxygen it forms a series of oxides and oxacids, as follows :—

CHLORINE OXIDES		CHLORINE OXACIDS	
Chlorine monoxide, or	} $\text{Cl}_2\text{O}$	Hypochlorous acid	. $\text{HClO}$
hypochlorous oxide		Chlorous acid	. . . $\text{HClO}_2$
Chlorine trioxide, or	} $\text{Cl}_2\text{O}_3$	Chloric acid	. . . $\text{HClO}_3$
chlorous oxide . .		Perchloric acid	. . . $\text{HClO}_4$
Chlorine tetroxide . .	$\text{Cl}_2\text{O}_4$		

*Hydrochloric Acid*,  $\text{HCl}$ , (muriatic acid, hydrogen chloride) may be prepared, as already shown, by the direct union of equal volumes of hydrogen and chlorine under the influence of light. It is, however, best procured in practice from the action of sulphuric acid on sodium chloride, sodium sulphate being left as a residue, thus :—



The hydrochloric acid is evolved as a gas, which is best collected by displacement. It is colourless, strongly acid, fuming in the air, and has a suffocating odour. It becomes liquefied by exposure to a pressure of about forty atmospheres. Hydrochloric acid gas is very soluble in water, that liquid taking up 480 times its own bulk at ordinary temperatures, forming a colourless solution which fumes strongly in the air. The solution constitutes the liquid acid of commerce, which is largely used in chemical manufactures, in metallurgy, and as a re-agent in the laboratory. The strongest hydrochloric acid has a specific gravity of 1.21, and contains about

42 per cent. of real acid. On the application of heat it loses strength, from the expulsion of hydrochloric acid gas, the boiling point of the liquid becoming finally constant at  $110^{\circ}$ , when an acid distils over, which contains 20.22 per cent. of HCl. If a weaker solution is distilled, it becomes concentrated by losing water until the liquid in the retort has reached the strength named. It has, however, been shown that the composition of the liquid obtained varies with the barometric pressure, so that it cannot be regarded as a chemical compound of water and hydrochloric acid gas. The same argument applies to some other acids which form similar combinations with water. The principal source of the hydrochloric acid of commerce is as a by-product from alkali works (see SODIUM CARBONATE). The acid obtained from this source is, however, very impure, but can be purified without difficulty by distillation. The chief commercial use of hydrochloric acid is in the preparation of chlorine, and as a solvent for some of the metals. Mixed with nitric acid, it forms the so-called "aqua-regia," which has the property of dissolving gold and platinum, metals which are unaffected by either hydrochloric or nitric acid if used separately. Aqua-regia will also attack certain sulphides, which cannot be acted on by the use of any ordinary acid used singly. The great solvent action of aqua-regia appears to be due to its powers of oxidation. The oxygen of the nitric acid unites with the hydrogen of the hydrochloric acid to form water, while chlorine is liberated in the nascent condition, and unites with the metals present to form soluble chlorides.

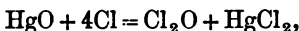
The composition of hydrochloric acid admits of easy demonstration, both synthetically and analytically.\*

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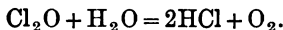
\* The term *synthesis* means a putting together, and is used to express the formation of a compound by bringing its components together. *Analysis*, on the other hand, is used to express the determination of the composition of a substance by breaking it up into its constituents.

Equal volumes of chlorine and hydrogen combine to form hydrochloric acid without change of volume; while, if a piece of potassium is heated in hydrochloric acid gas, potassium chloride is formed, and hydrogen set free, and the bulk of this hydrogen amounts to exactly half the original volume of gas. Solution of hydrochloric acid submitted to electrolysis yields chlorine and hydrogen in equal volumes.

*Chlorine Monoxide, or Hypochlorous Oxide*,  $\text{Cl}_2\text{O}$ , is prepared by the action of chlorine on mercuric oxide—



in which chlorine monoxide and mercuric chloride are formed. Chlorine monoxide is a gas of a pale reddish-yellow colour and peculiar odour. It is exceedingly unstable, and cannot be preserved even for a few hours without partial decomposition. It will sometimes decompose so rapidly that explosion occurs. By the action of a freezing mixture, chlorine monoxide may be condensed to a deep red liquid, which is unstable and explosive. The gas possesses most powerful bleaching properties—more powerful, indeed, than those of chlorine. This is due to the fact that the hypochlorous oxide yields up its own oxygen in the nascent condition, at the same time that the oxygen in a molecule of water is liberated in the same condition, thus :—



Hypochlorous oxide is dissolved by water, with which it unites to form hypochlorous acid.

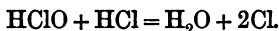
*Hypochlorous Acid*,  $\text{HClO}$ , may be prepared as above, but is more easily procured by less direct means. When a current of chlorine gas is passed into a cold dilute solution of an alkali, a hypochlorite is formed, together with a chloride, thus :—



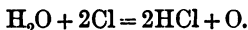
*The solution thus obtained yields a solution of hypo-*

chlorous acid on distillation with dilute nitric acid. The aqueous solution of hypochlorous acid has a yellowish colour, acrid taste, and peculiar odour. In the concentrated condition it decomposes rapidly, but when dilute it is more stable. It has powerful bleaching properties, and in the dilute condition may be used to destroy ink-marks, which it effects without damaging the paper.

When hypochlorous acid is acted on by hydrochloric acid, the following reaction occurs :—



The chlorine in both acids is thus liberated in the free state. The most important compound of hypochlorous acid is that which it forms with calcium, and which is the active ingredient of ordinary bleaching powder. This is prepared by passing chlorine gas into chambers containing slaked lime. A peculiar compound is formed, to which the formula  $\text{CaCl}_2 \cdot \text{Ca}_2\text{ClO}$  has been assigned. This splits up on the addition of water forming calcium chloride, and calcium hypochlorite. In bleaching ordinary goods, they are first soaked in a clear solution of bleaching powder, after which they are taken out, and immersed in dilute acid, a process termed souring, which has the effect of liberating chlorine, and the liberated chlorine reacts on the water present, thus :—



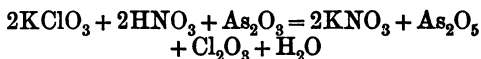
The oxygen thus evolved in a nascent state in the fibres of the material, oxidises the colouring matters present, producing colourless oxidation products, and thus bleaching.

When chloride of lime is acted on by a weak acid, such as very dilute sulphuric acid, hypochlorous acid is set free by the decomposition of the calcium hypochlorite present; if, however, a stronger acid be used, calcium chloride and hypochlorite are decomposed.



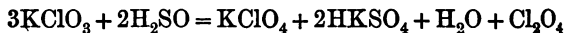
simultaneously, and the liberated hydrochloric and hypochlorous acids react on each other (as already shown) with formation of water and free chlorine. A very weak acid, such as carbonic acid, is sufficient to liberate hypochlorous acid from chloride of lime, so that the simple suspension in a room, of cloths saturated in the solution, is often sufficient for disinfecting purposes, sufficient decomposition ensuing from the carbonic acid present. Where a more powerful disinfecting action is required, it is best to expose saucers full of the chloride of lime, mixed with a dilute mineral acid.

*Chlorine Trioxide, or Chlorous Oxide,  $\text{Cl}_2\text{O}_3$ ,* may be prepared by heating a mixture of potassium chlorate, arsenious acid, and nitric acid, in a flask in the water bath.



The flask should be completely filled with the materials. Chlorous oxide is a greenish-yellow gas, which may be condensed by the use of a freezing mixture to a deep red-brown liquid, which explodes on an elevation of temperature. It is decomposed by water forming chlorous acid. Chlorous acid,  $\text{HClO}_2$ , prepared as above, possesses powerful bleaching properties, and unites with bases to form chlorites.

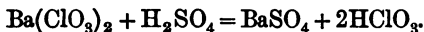
*Chlorine Tetroxide,  $\text{Cl}_2\text{O}_4$ ,* may be obtained by the action of sulphuric acid on potassium chlorate by the aid of a gentle heat.



Chlorine tetroxide is a dark-yellow gas of a powerful odour. Its preparation requires the greatest care, as it explodes violently at a temperature below that of boiling water. It does not appear to form distinct salts, but gives mixtures of chlorites and chlorates.

*Chloric Acid,  $\text{HClO}_3$ ,* is best prepared from a solution

of one of its compounds—barium chlorate—by addition of dilute sulphuric acid. Insoluble barium sulphate is formed, and chloric acid set free, thus :—



The dilute solution of chloric acid thus obtained may be concentrated by cautious evaporation. After concentration, it is a colourless syrupy liquid, possessing powerful oxidising properties, and readily suffering decomposition by contact with oxidisable substances. Chloric acid may be easily prepared in a combined state by passing chlorine gas through a strong warm solution of caustic potash, when the following reaction occurs :—

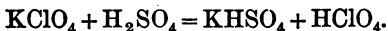


in which six equivalents of caustic potash and six of chlorine yield five equivalents of potassium chloride, and one of potassium chlorate. On the basis of this equation, it is easy to calculate what amount of potassium chlorate can be obtained from a given quantity of chlorine. Supposing, for instance, it is required to ascertain how many pounds of potassium chlorate can be produced from 133·1 lbs. of chlorine, using the requisite quantity of caustic potash. Now, in the equation, six equivalents of  $\text{Cl} = 35\cdot5 \times 6 = 213$  parts yield one equivalent of  $\text{KClO}_3 = 122\cdot6$  parts, and the sum is therefore expressed as follows :—

$$\begin{array}{ccccccc} 213 & : & 133\cdot1 & :: & 122\cdot6 & : & x \\ & & & & x = 76\cdot6\text{lbs.} & & \text{KClO}_3. \end{array}$$

The chlorates yield oxygen on being heated, suffering conversion into chlorides.

**PERCHLORIC ACID**,  $\text{HClO}_4$ , is prepared by carefully distilling potassium perchlorate with sulphuric acid.



It is a colourless liquid, liable to explode spontaneously. It possesses very intense oxidising properties, and con-

tact with charcoal, or any organic substance, is sufficient to cause it to explode. In combination, perchloric acid may be prepared by heating a chlorate to a certain stage. If, for instance, potassium chlorate is moderately heated, it first fuses and evolves oxygen, and then temporarily solidifies, when the application of heat should be stopped. The following reaction takes place :—



in which two equivalents of potassium chlorate yield one of potassium perchlorate and one of potassium chloride, free oxygen being at the same time given off. Aqueous perchloric acid is the most stable of the chlorine acids.

Appended is a table, showing concisely the modes of preparation and leading characteristics of the oxides of chlorine :—

[Table

*Table showing the Methods of Preparation and Leading Characteristics of the Oxides and Oxacids of Chlorine:—*

NAME	FORMULA	MODE OF PREPARATION	LEADING CHARACTERISTICS
Chlorine Monoxide or Hypochlorous Oxide.	$\text{Cl}_2\text{O}$	By the action of chlorine on mercuric oxide. $\text{HgO} + 4\text{Cl} = \text{Cl}_2\text{O} + \text{HgCl}_2$	Colourless gas, condensed by a freezing mixture to a red, unstable liquid, liable to separation into its constituent elements, with explosion.
Chlorine Trioxide or Chlorous Oxide.	$\text{Cl}_2\text{O}_3$	By heating a mixture of potassium chlorate, arsenious acid, and nitric acid in a flask in the water bath. $2\text{KClO}_3 + 2\text{HNO}_3 + \text{As}_2\text{O}_3 = 2\text{KNO}_3 + \text{As}_2\text{O}_6 + \text{Cl}_2\text{O}_3 + \text{H}_2\text{O}$	Greenish yellow gas, unstable, and explosive, liquefiable by extreme cold, forms chlorous acid with water.
Chlorine Tetroxide or Chloric Peroxide.	$\text{Cl}_2\text{O}_4$ or $\text{ClO}_2$	By the action of sulphuric acid on potassium chlorate with the aid of a gentle heat. $2\text{KClO}_3 + 2\text{H}_2\text{SO}_4 + \text{KClO}_4 = 2\text{HKS O}_4 + \text{H}_2\text{O} = \text{Cl}_2\text{O}_4$	Dark yellow gas, very unstable, and liable to explosion, condensed by cold to a brown-red liquid; is soluble in water.
Hypochlorous Acid.	$\text{HClO}$	By the action of hypochlorous oxide on water $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HClO}$ . Also by distilling a hypochlorite with dilutenitric acid.	Colourless liquid of peculiar odour, possesses powerful bleaching properties; forms hypochlorites with bases.

Table—(Continued)

NAME	FORMULA	MODE OF PREPARATION	LEADING CHARACTERISTICS
Chlorous Acid.	$\text{HClO}_2$	By acting on chlorous oxide with water. $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HClO}_2$	Greenish yellow liquid, possessing oxidising and bleaching properties; forms chlorites with bases.
Chloric Acid.	$\text{HClO}_3$	By decomposing barium chlorate with dilute sulphuric acid. $\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HClO}_3$ and subsequently concentrating the solution by cautious evaporation.	Syrupy liquid, of powerful oxidising properties; forms chlorates with bases.
Perchlorate Acid.	$\text{HClO}_4$	By carefully distilling potassium perchlorate with strong sulphuric acid. $\text{KClO}_4 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HClO}_4$	Colourless fuming liquid of specific gravity 1.78; one of the most powerful oxidising substances known; forms perchlorates with bases, and forms a thick oily hydrate with water.

CHLORINE

## BROMINE

SYMBOL, Br.

COMBINING WEIGHT, 80

Derives its name from "*Brōmos*," a stench, and was discovered by Balard in 1826 from the salts obtained from the evaporation of sea-water.

**PREPARATION.**—Bromine is generally obtained from the saline residue obtained from the evaporation of the water of certain springs which contain small quantities of bromide of magnesium. A celebrated spring of this kind is that at Kreuznach, in Prussia. In the preparation of bromine advantage is taken of the fact that chlorine will liberate this element from bromides, a displacement occurring in which the chlorine takes the place of the bromine which is set free. The mother liquor obtained from the evaporation of a water charged with bromides is treated with a stream of chlorine. The chlorine liberates the bromine from its combinations; and agitation with ether dissolves the bromine thus set free, forming a bright red solution. The ethereal solution is then removed from the exhausted mother liquor, and caustic potash added, when the colour immediately disappears from the combination of the bromine with the potash—potassium bromide and potassium bromate being formed. The solution is then evaporated to dryness, ignited to redness to convert the bromate present into bromide; and, finally, the salt eventually obtained is distilled in a small retort together with manganese dioxide, sulphuric acid, and a little water. The end of the retort is made to dip into cold water, and the bromine distils over, condensing in drops beneath the surface of the water. The action which occurs in the distillation is as follows:—

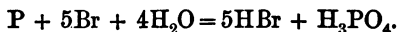


**PROPERTIES.**—Bromine is a thin, dark-red liquid of an intense colour and insupportable odour. It is the only liquid element, except mercury. Its specific gravity

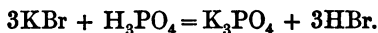
at 4° is 2.966; it freezes at —22° to a black-looking solid, and boils at 63°. It is slightly soluble in water, more freely in alcohol, and abundantly in ether. The aqueous solution like that of chlorine possesses bleaching properties.

PRINCIPAL COMPOUNDS.—The most important compounds of bromine are hydrobromic and bromic acids corresponding in composition to the similar chlorine acids. Hypobromous acid, corresponding to hypochlorous acid, is also known, and likewise perbromic acid corresponding to perchloric acid. The analogous compound to  $\text{Cl}_2\text{O}$  is, however, not known.

HYDROBROMIC ACID,  $\text{HBr}$ .—Unlike chlorine, bromine will not unite with hydrogen at ordinary temperatures even in direct sunlight; combination, however, ensues if the mixed gas and vapour are subjected to a red heat. Hydrobromic acid is, however, better prepared by the action of such an acid as phosphoric on a bromide, or by bringing bromine and phosphorous in contact with water when a violent action occurs, phosphoric and hydrobromic acids being formed:—

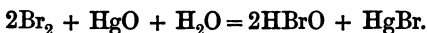


The preparation of hydrobromic acid from potassium bromide by the action of phosphoric acid may be illustrated thus:—



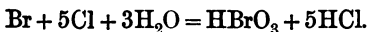
Hydrobromic acid resembles hydrochloric acid in its properties being an invisible gas, fuming strongly in the air, very soluble in water, and uniting with bases to form a class of salts called bromides. The gas liquefies at a temperature of —73°, and an aqueous solution containing 47 per cent. of  $\text{HBr}$  boils at 126°. Bromides of the alkalis may be easily prepared by saturating the respective bases in solution with bromine, evaporating to dryness, and igniting to decompose any bromate *which may be present*.

*Hypobromous Acid*,  $\text{HBrO}$ , is obtained by the action of mercuric oxide on bromine water, thus :—



The acid possesses bleaching properties, and unites with calcium to form a compound resembling calcium hypochlorite, the active ingredient of ordinary bleaching powder.

**BROMIC ACID**,  $\text{HBrO}_3$ , resembles chloric acid in its properties, and is best prepared by acting on bromine water with chlorine :—



By the saturation of the respective alkalies with bromine, bromates and bromides are formed, thus :— $6\text{Br} + 6\text{KHO} = \text{KBrO}_3 + 5\text{KBr} + 3\text{H}_2\text{O}$ . The two compounds, may be separated by crystallisation. The bromates, like the corresponding chlorates, yield oxygen on being heated, and are converted into bromides.

*Perbromic Acid*,  $\text{HBrO}_4$ , has been obtained by the action of bromine or perchloric acid.

Following is a table of the preparation and properties of the oxides and oxacids of bromine :—

[TABLE



*Table showing the Methods of Preparation and Leading Characteristics of the Oxides and Oxacids of Bromine :—*

NAME	FORMULA	METHOD OF PREPARATION	LEADING CHARACTERISTICS
Hypobromous Acid.	$\text{HBrO}$	By the action of mercuric oxide on bromine water— $2\text{Br}_2 + \text{HgO} + \text{H}_2\text{O} = 2\text{HBrO} + \text{HgBr}_2$	Unstable ; chiefly characterised by its bleaching properties ; forms hypobromites with bases resembling the corresponding hypochlorites.
Bromic Acid.	$\text{HBrO}_3$	By acting on bromine water with chlorine— $\text{Br} + 5\text{Cl} + 3\text{H}_2\text{O} = \text{HBrO}_3 + 5\text{HCl}$	Resembles chloric acid in its properties ; forms bromates with bases.
Perbromic Acid.	$\text{HBrO}_4$	By the action of bromine on perchloric acid.	

## IODINE

SYMBOL, I.

COMBINING WEIGHT, 127

IODINE derives its name from "*iodēs*" (violet coloured), from the colour of its vapour, and was discovered by M. Courtois of Paris, in 1812.

PREPARATION.—The greater part of the iodine of commerce is obtained from Kelp, the half-vitrified ashes of sea-weeds, in which it exists as the iodides of sodium and magnesium. The sea-weed seems to possess a property of abstracting the iodine from sea-water, and accumulating it in its tissues. In procuring iodine from kelp, the latter substance is dissolved in water, the solution concentrated to a small bulk, the more crystallisable salts removed, and finally, the dark mother liquor which is left is treated with manganese dioxide and sulphuric acid, and distilled. The action which occurs is exactly the same as in the case of the preparation of bromine.

PROPERTIES.—Iodine is a solid of a bluish black colour, which, as generally met with in commerce, is in the form of crystalline plates or scales, having an imperfect metallic lustre resembling that of plumbago.

The specific gravity of iodine is 4.948; \* it melts at 107°, and boils at between 175° and 180°, yielding a vapour of an exceedingly beautiful violet colour. It is very sparingly soluble in pure water, but is freely dissolved in the presence of the iodides of the alkali metals or of hydriodic acid. Iodine is also dissolved by alcohol and ether, with which it forms brown liquids. It is also very freely soluble in chloroform and bisulphide of carbon, giving solutions of a fine violet colour. Iodine resembles chlorine and bromine in its chemical characteristics, with the exception that neither it nor

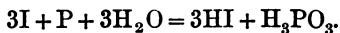
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\* The specific gravity of solids, like that of liquids, is the weight of a unit bulk of material compared with an equal bulk of water.

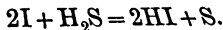
any of its compounds exhibit bleaching properties. It is likewise somewhat less active in combination, being capable of displacement by either chlorine or bromine. One of the most characteristic reactions of free iodine is the formation of a splendid blue colour with starch. If a little starch paste is added to a small quantity of a solution of a soluble iodide no reaction takes place until the iodine is liberated from its combination by the addition of a little chlorine water, when a beautiful blue is produced.

**PRINCIPAL COMPOUNDS.**—The most important compounds of iodine are hydriodic and iodic acids; periodic acid is also known, as well as two oxides—the pentoxide and heptoxide. It also forms a remarkable compound with nitrogen, and unites with chlorine to form several chlorides.

**HYDRIODIC ACID, HI.**—Iodine combines directly with hydrogen by the agency of heat, but hydriodic acid is better prepared by acting on phosphorus triiodide with water when hydriodic and phosphorous acids are formed, or more simply from the direct action of phosphorus on iodine. The two substances react energetically on each other, and the experiment is best performed by placing in a test tube—firstly, a little iodine, then some roughly pounded glass moistened with water, then a few fragments of phosphorus followed by more glass, and repeating the arrangement until the tube is about half full. The application of a gentle heat then causes the formation of hydriodic acid, which is evolved as a gas—

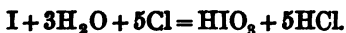


An aqueous solution of hydriodic acid may be very simply prepared by suspending iodine in fine powder in water, and passing a stream of sulphuretted hydrogen through the mixture, when the following reaction takes place :—



When the solution has become colourless, it is gently heated to expel the excess of sulphuretted hydrogen, and filtered to remove the suspended sulphur. Hydriodic acid is very similar in its character to the corresponding acid of chlorine, being a colourless gas which rises in the air, and is very soluble in water. It may be liquefied by pressure, and solidifies at  $-55^{\circ}$ . The aqueous solution containing 57 per cent. of HI, boils at  $127^{\circ}$ . The superior affinity of hydrogen for oxygen to that which it has for iodine, renders hydriodic acid a powerful reducing agent.

Iodic Acid,  $\text{HIO}_3$ , corresponding to chloric acid,  $\text{HClO}_3$ , may be prepared by the direct oxidation of iodine with nitric acid or chlorine. Solid iodine may be boiled for some time with strong nitric acid, or a current of chlorine gas may be passed through iodine water. The action which occurs in the latter case is as follows:—



By the evaporation of the solution the iodic acid is left as a white mass which may be purified by solution in water and crystallisation. When pure it forms white hexagonal tablets, having the composition  $\text{H}_2\text{O}, \text{I}_2\text{O}_5 + 2\text{H}_2\text{O}$ . At  $130^{\circ}$  two equivalents of water are expelled, while at a temperature of  $176^{\circ}$  the whole of the water is driven off, and iodine pentoxide, or anhydrous iodic acid, as it is sometimes called ( $\text{I}_2\text{O}_5$ ), is left.

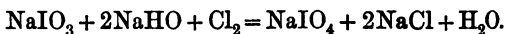
Alkaline iodates may be procured like the corresponding chlorates and bromates by treating the caustic alkalies with iodine, when iodides and iodates are simultaneously formed. If an excess of caustic alkali be employed, and chlorine afterwards passed through the solution, the whole of the iodine is converted into iodic acid, thus:—



From this reaction it would appear that the affinity

of oxygen for iodine is greater than for chlorine, for an iodate is formed in preference to a chlorate. The alkaline iodates, like the corresponding chlorates and bromates, yield oxygen on being heated, and are converted into iodides.

PERIODIC ACID,  $\text{HIO}_4$ , may be procured by acting on perchloric acid with iodine. It is a white crystalline solid. The periodates of potash or soda may be formed by passing chlorine through an alkaline solution of the corresponding iodate, thus :—



IODINE PENTOXIDE,  $\text{I}_2\text{O}_5$ , is formed by heating iodic acid to  $170^\circ$ . It is a white crystalline solid.

IODINE HEPTOXIDE,  $\text{I}_2\text{O}_7$ , a white substance obtained by heating periodic acid to  $170^\circ$ .

Appended is a table of the preparation and properties of the oxides and oxacids of iodine.

{TABLE

*Oxids and Oxacids of Iodine:—*

NAME	FORMULA	METHOD OF PREPARATION	LEADING CHARACTERISTICS
Iodic Acid	$\text{HIO}_3$	By the direct oxidation of iodine with nitric acid or chlorine. $\text{I} + 3\text{H}_2\text{O} + 5\text{Cl} = \text{HIO}_3 + 5\text{HCl}$	White solid substance crystallising from its aqueous solution in hexagonal tablets containing. $\text{H}_2\text{O}, \text{I}_2\text{O}_5 + 2\text{H}_2\text{O}$ Forms iodates with bases.
Periodic Acid	$\text{HIO}_4$	By the action of iodine on perchloric acid.	White crystalline solid, crystallising from its aqueous solution in prismatic crystals. $\text{H}_2\text{O}, \text{I}_2\text{O}_7, 4\text{H}_2\text{O}$ Forms periodates with bases.
Iodine Pentoxide	$\text{I}_2\text{O}_5$	By heating iodic acid to $170^\circ$ .	White crystalline solid.
Iodine Heptoxide	$\text{I}_2\text{O}_7$	By heating periodic acid to $170^\circ$ .	Little known.

## FLUORINE

SYMBOL, F

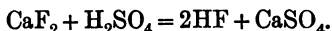
COMBINING WEIGHT, 19

DISTRIBUTION.—Occurs in nature in the combined state only, principally as calcium fluoride or fluorspar,  $\text{CaF}_2$ , found in Derbyshire, and as cryolite, a double fluoride of sodium, and aluminium, met with in Greenland.

PREPARATION AND PROPERTIES.—It is somewhat doubtful whether fluorine in the free condition has ever been obtained. By the action, however, of dry iodine on dry silver fluoride, a gaseous body, believed to be fluorine, has been produced. It is said to somewhat resemble chlorine in its properties.

## PRINCIPAL COMPOUNDS

HYDROFLUORIC ACID,  $\text{HF}$ .—A gaseous body obtained by the action of sulphuric acid upon calcium fluoride, thus:—



To a great extent it resembles the corresponding hydrogen compounds of chlorine, bromine, and iodine in its properties, being a colourless gas, fuming strongly in the air. It is doubtful whether hydrofluoric acid has ever been prepared entirely free from water. As evolved from fluorspar by the action of sulphuric acid, it can be condensed to a liquid by exposure to a cold of  $-20^\circ$ . This liquid is really a strong aqueous solution of the acid, it evolves suffocating fumes when exposed to the air, hisses when mixed with water, and produces painful ulcers if dropped upon the skin. When diluted so as to contain 36 per cent. of  $\text{HF}$ , the acid has a constant boiling point of  $120^\circ$ . A characteristic property of hydrofluoric acid is that it combines *energetically* with sulphur trioxide ( $\text{SO}_3$ ) and phos-

phorus pentoxide ( $P_2O_5$ ) with great evolution of heat. Its most distinguishing characteristic is, however, the corrosive action which it exercises on glass. Dry hydrofluoric acid gas has little or no action on glass, but in the presence of moisture the silica of the glass unites with the fluorine of the hydrofluoric acid to form a volatile body called silicon tetrafluoride. (See SILICON.) The acid cannot consequently be prepared in glass vessels, vessels of lead being always used. The corrosive property of hydrofluoric acid is utilised for the purpose of etching on glass. For this purpose the glass is covered with wax, the design traced with a pointed instrument so as to penetrate the wax, and expose the naked surface of the glass, which is then submitted to the action of the acid, preferably in the form of vapour. After a time the glass is removed, the wax taken off with the assistance of a little oil of turpentine, and the design is then found engraved on the glass. This property of acting on glass serves as a useful test for the presence of fluorine. Calcium fluoride is largely used as a flux in metallurgical operations. Chlorine, bromine, iodine and fluorine, form a group generally spoken of as "the halogens," and possessing great similarity in many of their properties, and more especially in their compounds. The appended tables show concisely the general properties and characteristics of the halogens, and the properties and distinctive tests of their hydracids.

[TABLE



*Table showing the General Characteristics and Distinctive Tests of the Hydracids of the Halogens*

NAME	SYMBOL	ATOMIC WEIGHT	GENERAL CHARACTERISTICS	DISTINCTIVE TESTS
Hydrofluoric acid .	HF	20	Colourless gas, fuming strongly in the air; very soluble in water, and condensing at $-20^{\circ}$ to a colourless liquid; aqueous solution boils at $120^{\circ}$ , and contains 37 per cent. of HF; possesses the property of etching glass.	With solution of $\text{AgNO}_3$ , soluble fluoride. Free HF etches glass when moisture is present.
Hydrochloric acid .	HCl	36.5	Resembles the previous compound in physical characteristics; condenses by a pressure of 40 atmospheres to a colourless liquid. The aqueous solution of specific gravity 1.21 contains 48 per cent. of HCl.	With solution of $\text{AgNO}_3$ , white curdy precipitate of silver chloride, insoluble in water and $\text{HNO}_3$ , soluble in $\text{NH}_3$ .
Hydrobromic acid .	HBr	81	Resembles previous compounds in physical properties; liquefies at $-71^{\circ}\text{C}$ .	With solution of $\text{AgNO}_3$ , white precipitate, soluble with difficulty in ammonia, insoluble in $\text{HNO}_3$ .
Hydriodic acid .	HI	128	Resembles previous compounds in physical properties; liquefies by pressure and solidifies at $-55^{\circ}\text{C}$ .	With solution of $\text{AgNO}_3$ , yellowish-white precipitate, insoluble in ammonia and $\text{HNO}_3$ . With a little $\text{HNO}_3$ and starch paste, a blue colour.

Table showing the Leading Characteristics of the Halogens.

NAME	SYMBOL	ATOMIC WEIGHT	SPECIAL CHARACTERISTICS	GENERAL CHARACTERISTICS
Fluorine	F	19	Supposed to be a gaseous body resembling chlorine.	The halogens exhibit a regular gradation in physical properties, and in their atomic weights, their chemical energies are in the inverse ratio of their atomic weights. They all unite with hydrogen in the proportion of one volume of the halogen in vapour to one volume of hydrogen to form two volumes of a gaseous acid. These acids are characterised by possessing a powerful attraction for moisture, being very soluble in water, and having a great similarity of odour. They all form well marked salts, the potassium salts crystallising in the same form (cubical); the silver compound of fluorine is, however, soluble in water, while those of chlorine, bromine, and iodine, are insoluble.
Chlorine	Cl	35.5	Greenish yellow gas of suffocating odour; slightly soluble in water; aqueous solution possesses bleaching properties	
Bromine	Br	80	Deep red volatile liquid of suffocating odour; boils at 63°C., and freezes at 22°C.; has a specific gravity of 2.966 at 4°; slightly soluble in water; aqueous solution, possesses bleaching properties.	
Iodine	I	127	Dark steel grey solid of specific gravity 4.95, melts at 115° and boils above 200°, yielding a violet coloured vapour; slightly soluble in water; forms a characteristic blue compound with starch.	

## SULPHUR

SYMBOL, S

COMBINING WEIGHT, 32

DISTRIBUTION.—Sulphur occurs in nature in the free state, in combination with metals as sulphides, and with metals and oxygen as sulphates. In the free condition, sulphur is found in volcanic regions, the beds at Sicily being the most productive and best known. The sulphur occurs in a matrix of rock-salt, gypsum, and celestine. In combination with metals, sulphur occurs as iron and copper pyrites, zinc sulphide or Blende, and lead sulphide or Galena, besides several rarer compounds. As sulphates, sulphur occurs principally as calcium sulphate or gypsum, barium sulphate or heavy spar; while sodium sulphate or Glauber's salt, and magnesium sulphate or Epsom salts, are common ingredients of mineral waters. Sulphur also occurs in combination with oxygen, as sulphurous oxide in volcanic emanations, and in combination with hydrogen as sulphuretted hydrogen, found in certain mineral waters, as at Harrogate. Sulphur is found in small quantities in most bituminous coals, and in certain organic compounds, such as albumen, cystine, taurine, and the alliaceous volatile oils.

PREPARATION.—Sulphur is generally procured from those ores which contain the element in the free state. The first crude product is often obtained by a very wasteful process, rough heaps of the ore being set on fire, the heat of the combustion of a portion of the sulphur fusing the rest. It can be more economically prepared by heating the crude material in closed earthen pots or retorts, when the sulphur distils over in a comparatively pure form, and is condensed and received in vessels placed outside the furnace. The sulphur so obtained is sometimes re-melted and cast *into sticks*, in which form it is known as "roll sul-

phur," or "stick brimstone." A still purer form is produced by distilling the half-purified material, and receiving the vapour in a large brick chamber, where the sulphur condenses as a fine powder, which is known in commerce as "flowers of sulphur," or "sublimed sulphur." Sulphur is also occasionally prepared from copper or iron pyrites, as a preliminary to the separation of the respective metals from their ores. The ore is packed in large heaps with brushwood and ignited, when part of the sulphur burns away, and part is fused and flows from the heap. Sulphur is also obtained from the waste of alkali works, and from the spent oxide of iron from gas-works, which has been used for the extraction of sulphuretted hydrogen from the crude gas.

PROPERTIES.—Sulphur is a brittle solid, of a lemon-yellow colour, tasteless, and almost odourless. It is inflammable, and burns with a bluish flame, the sole product of combustion being sulphurous oxide,  $\text{SO}_2$ . It is fusible, and boils at  $440^\circ$ , giving off an orange-coloured vapour. Sulphur exists in three "allotropic" forms, known respectively as sulphur alpha, beta, and gamma. The first of these, the crystalline, is that in which it occurs in nature; the remaining two modifications are obtained by fusion. Native sulphur crystallises in rhombic pyramids. Its specific gravity is 2.05, and its melting point  $114.5^\circ \text{C}$ . The second modification is obtained when ordinary sulphur is fused and allowed to cool slowly, when it crystallises in long, needle-shaped, prismatic crystals, which have a specific gravity of 1.98, and melting point of  $120^\circ \text{C}$ . These crystals, on keeping, become opaque, from undergoing a spontaneous change to the ordinary form or natural variety. Both these varieties of sulphur dissolve freely in carbon disulphide and in turpentine, and the solutions so obtained deposit crystals of the ordinary variety on evaporation. The third modification of sulphur is obtained by pouring melted sulphur at a temperature

of  $230^{\circ}\text{C}$ . into cold water, when it forms a soft, tenacious, semi-transparent mass, of specific gravity 1.96, which is insoluble in carbon disulphide. This form of sulphur is not permanent, and changes in a few hours at ordinary temperatures to the usual native form; while if heated to  $100^{\circ}\text{C}$ . the change is instantaneous, the temperature rising to  $110^{\circ}\text{C}$ . The changes which ordinary sulphur undergoes when exposed to heat are peculiar. At  $114.5^{\circ}$  it melts, and at  $120^{\circ}$  forms a thin yellow liquid. As the temperature rises it becomes dark-coloured and viscid, until at about 200 to  $250^{\circ}$ . At this point the flask in which it is contained may be inverted for a short time without the sulphur flowing out. A further increase of temperature renders the mass again thin and liquid, a condition which is maintained until the boiling point is reached at  $440^{\circ}$ .

*Table showing Effect of Heat on Sulphur; Electro-positive converted into Electro-negative, latent heat becoming sensible during the process.*

SULPHUR—SOLID

Yellow . . . . .	$120^{\circ}$ Liquid
Brown, nearly black about	$230^{\circ}$ Viscid; heat here becomes latent.
"                    "	$300^{\circ}$ Again liquid
Brownish-red . . . .	$440^{\circ}$ Boils; vapour given off.

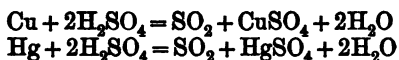
Sulphur unites readily with most of the other elements, whilst many of the metals burn in its vapour, forming sulphides.

COMPOUNDS OF SULPHUR AND OXYGEN.—Two compounds of sulphur and oxygen are known in the free state, both of which form oxacids when acted on by water—viz., sulphur dioxide or sulphurous oxide,  $\text{SO}_2$ , and sulphur trioxide or sulphuric oxide,  $\text{SO}_3$ , which, by union with water, form the oxacids,  $\text{H}_2\text{SO}_3$ , or sulphurous acid, and  $\text{H}_2\text{SO}_4$ , or sulphuric acid. The remaining compounds of oxygen and sulphur are only known in the form of their oxacids. The whole series, arranged systematically, are as follow :—

HYDROSULPHUROUS ACID	.	.	$\text{H}_2\text{SO}_2$
SULPHUROUS ACID	.	.	$\text{H}_2\text{SO}_3$
SULPHURIC ACID	.	.	$\text{H}_2\text{SO}_4$
HYPOSULPHUROUS ACID	.	.	$\text{H}_2\text{S}_2\text{O}_3$
DITHIONIC ACID	.	.	$\text{H}_2\text{S}_2\text{O}_6$
TRITHIONIC ACID	.	.	$\text{H}_2\text{S}_3\text{O}_6$
TETRATHIONIC ACID	.	.	$\text{H}_2\text{S}_4\text{O}_6$
PENTATHIONIC ACID	.	.	$\text{H}_2\text{S}_5\text{O}_6$

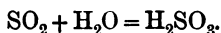
The second, third, and fourth numbers of the series are the only ones of commercial importance, the remaining compounds being merely of scientific interest.

**SULPHUR DIOXIDE, OR SULPHUROUS OXIDE,  $\text{SO}_2$ .—**  
This compound is formed when sulphur or combustible bodies containing sulphur are burnt in the air. The most convenient mode of preparation is by acting on sulphuric acid,  $\text{H}_2\text{SO}_4$ , by means of a metal, such as copper or mercury, when oxygen is withdrawn, and sulphurous oxide, together with water, is evolved:—



Sulphurous oxide is also produced by heating together charcoal and sulphuric acid, sulphurous oxide and carbon dioxide being formed. The gas must be passed through a small quantity of water, in order to wash it, and may then be collected over mercury, or by displacement. Sulphurous oxide gas is colourless and transparent, possessing the peculiarly suffocating smell of burning sulphur. It is a non-supporter of combustion. Exposed to a temperature of  $-10^\circ$ , it condenses to a colourless liquid, which, at below  $-76^\circ$ , freezes to a transparent solid. Sulphurous oxide may likewise be liquefied at common temperatures by a pressure of about three atmospheres. The liquid produces intense cold by its evaporation, as may be well shown by surrounding the bulb of an alcohol thermometer with cotton wool, and moistening it with the liquid, when

the temperature soon sinks to  $-60^{\circ}$ . Sulphurous oxide dissolves readily in water, one volume of which at a temperature of  $15^{\circ}$  absorbs 45 volumes of the gas. A solution is thus obtained of specific gravity 1.04, which has an acid reaction, and possesses the characteristic odour of the gas. On boiling the liquid, the dissolved sulphurous oxide is expelled. Sulphurous acid,  $\text{H}_2\text{SO}_3$ , is produced whenever sulphurous oxide is brought into contact with water—



It is also formed during the combustion of bodies containing hydrogen and sulphur. The saturated solution obtained by passing sulphurous oxide into water is in reality a solution of sulphurous acid, from which a crystalline hydrate, having the composition  $\text{H}_2\text{SO}_3 + 14\text{H}_2\text{O}$ , may be obtained on cooling the liquid to  $5^{\circ}$ . Sulphurous acid is dibasic, containing two atoms of hydrogen, replaceable by a base giving rise to two classes of salts, in the same way as carbonic acid. Sulphurous acid may be regarded as hydrogen sulphite, the acid potassium salt, or hydrogen potassium sulphite, having the formula  $\text{KHSO}_3$ , while the neutral salt or potassium sulphite is  $\text{K}_2\text{SO}_3$ .

Sulphurous oxide possesses bleaching properties, and is used largely in the arts for the bleaching of silk and wool. The sulphurous oxide used for this purpose is obtained by burning sulphur, or by acting on a sulphite by means of a stronger acid.

Sulphurous acid is likewise used as an "antichlor," for destroying the last traces of chlorine in materials which have been bleached by that substance, thus:—



The decolorising action of sulphurous oxide is due to an entirely opposite cause to that of chlorine. Chlorine, it will be remembered, acts by oxidation, forming *colourless* oxidation products with organic colouring

matters; sulphurous oxide, on the other hand, acts as a de-oxidising or reducing agent, uniting with the oxygen of an equivalent of water to form sulphuric acid; while the liberated hydrogen bleaches by reduction.

When exposed to direct sunlight, sulphurous oxide unites with an equal volume of chlorine to form a colourless liquid, having the composition  $\text{SO}_2\text{Cl}_2$ , and known as chloro-sulphuric acid or chloride of sulphuryl. Chloro-sulphuric acid is decomposed by water with formation of sulphuric and hydrochloric acid. Sulphuryl ( $\text{SO}_2$ ) is sometimes regarded as the radical of sulphuric acid, which may be written  $(\text{HO})_2\text{SO}_2$ , that is, sulphuryl united to two molecules of hydroxyl.

It has already been pointed out that the sole product of the combustion of sulphur in air, or in oxygen, is sulphurous oxide  $\text{SO}_2$ . With the knowledge of this fact, such a question as the following can be answered. A quantity of sulphur weighing four grams is burned in a close glass vessel containing 28.5 litres of pure dry air at  $27^\circ$  and 760 mm. What is the volume of gaseous mixture at  $0^\circ$  and 760 mm., and what is its composition per cent.?

Now sulphur, in uniting with oxygen to form  $\text{SO}_2$ , requires an equal weight of oxygen. 32 parts of sulphur, combining with  $16 \times 2 = 32$  parts of oxygen, 4 grams of S require, therefore, 4 grams of O to form 8 grams of  $\text{SO}_2$ . The volume of oxygen equal to 4 grams must then be found. A litre of O =  $0.8936 \times 16 = 1.4297$  grams, and 4 grams are equal, therefore, to—

$$1.4297 : 4 :: 1 : x$$

$$x = 2.798 \text{ litres}$$

Now 28.5 litres of air at  $27^\circ$  and 760 mm. equals 25.93 litres at  $0^\circ$  and the same pressure, and as pure dry air contains 20.9 per cent. by volume of oxygen, the volume of oxygen in the 25.93 litres is—

$$100 : 25.93 :: 20.9 : x$$

$$x = 5.419$$



And the amount of nitrogen is obviously the difference between the original volume 25·93, and  $5·419 - 2·798 = 2·621$ . Of the 5·419 litres of O, it has been calculated 2·798 litres would be required for union with sulphur, this would leave  $(5·419 - 2·798)$ , 2·621 of O remaining in the free state. We have, then arrived at the following data :—

Corrected volume of air = 25·93 litres.

This contains—

Nitrogen . . . . .	20·511	} 25·
Oxygen required for S = . . . . .	2·798	
Oxygen remaining in the free state	2·621	

The oxygen which combines with the sulphur to  $\text{SO}_2$  does so without change of volume, and the final mixture may, therefore, be written thus :—

Nitrogen . . . . .	20·511
Oxygen . . . . .	2·621
Sulphurous oxide ( $\text{SO}_2$ )	2·798
	<hr/>
	25·93 volume

of the gaseous mixture at  $0^\circ$  and  $760^\circ$ .

The composition of the gaseous mixture per cent can then be calculated thus, taking the percentage of nitrogen first :—

$$25·93 : 100 :: 20·511 : x$$

$$x = 79·1$$

Then for the oxygen :—

$$25·93 : 100 :: 2·621 : x$$

$$x = 10·10$$

Finally for the  $\text{SO}_2$  :—

$$25·93 : 100 :: 2·798 : x$$

$$x = 10·8$$

percentage composition of the gaseous mixture is as follows:—

Nitrogen . . .	79·1
Oxygen . . .	10·1
Sulphur dioxide	10·8
	<hr/>
	100·0

The principal use of sulphurous oxide is for the production of sulphuric acid, one of the most important chemical manufactures.

**SULPHUR TRIOXIDE**, or sulphuric anhydride,  $\text{SO}_3$ , (sometimes called anhydrous sulphuric acid).—This compound is best obtained by the distillation of Nordhausen sulphuric acid. Exposed to a gentle heat in a retort this substance evolves white fumes of sulphur trioxide, which may be condensed by passing them into a cooled receiver. Sulphur trioxide may

be prepared by passing sulphurous acid and oxygen, both in a perfectly dry condition, through a hot tube containing finely divided platinum. Sulphuric anhydride is a white crystalline solid, which is sufficiently soft to be moulded by the fingers. When recently solidified from the gaseous or liquid state it melts at about  $18^\circ\text{C}$ ., and boils at  $46^\circ\text{C}$ .

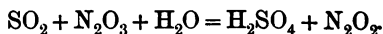
It does not redden dry litmus paper. Sulphuric anhydride hisses like a red hot iron when brought in contact with water, and forms sulphuric acid,  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ .

**SULPHURIC ACID**,  $\text{H}_2\text{SO}_4$ .—This important compound, which upwards of 100,000 tons are produced annually in this country, was first prepared by the distillation of ferrous sulphate or green vitriol. The acid prepared by this process is a mixture of sulphuric and sulphur trioxide.

It is still prepared on a small scale, mainly for dyeing indigo for use as a dye, and is known as *industrial sulphuric acid*, or Nordhausen acid from the

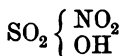
place in Saxony which is now the principal seat of its manufacture.

Ordinary sulphuric acid is prepared on a large scale by oxidising sulphurous acid in presence of the vapour of water by one of the lower oxides of nitrogen. The sulphurous acid produced from the combustion of sulphur or of pyrites is conducted into a series of large leaden chambers, to which are also admitted steam, air, and the vapour of nitric acid evolved from the action of sulphuric acid on a nitrate. A portion of the sulphurous acid is immediately converted into sulphuric acid by the vapour of nitric acid, which becomes reduced by loss of oxygen to nitric oxide. The nitric oxide so formed immediately takes up oxygen from the air being converted into nitrogen trioxide, which converts a further portion of sulphurous oxide into sulphuric acid, becoming again reduced to nitric oxide, thus:—



This action of the nitrogen compound of alternately giving up oxygen to convert sulphurous oxide into sulphuric acid, and taking up oxygen from the air goes on continuously so that the nitric oxide acts as a carrier or transferer of atmospheric oxygen, by which the conversion of sulphurous oxide into sulphuric acid is constantly proceeding. The leaden chambers in which the sulphuric acid is formed are connected with a tower containing coke wetted with oil of vitriol to arrest any products which may escape previous condensation. Finally, connection is made to a tall chimney in order to ensure a continuous current through the whole apparatus. Theoretically, a small quantity of nitrogen trioxide should be capable of converting in the presence of steam and air an indefinite amount of sulphurous oxide into the form of sulphuric acid; but in practice the nitrogen compound has to be continually supplied to the leaden chambers in small quantity. When the manufacture is progressing satis-

factorily, and the steam, air, sulphurous oxide, and nitric acid vapour are all being supplied in the proper proportions, nothing but nitrogen, together with a trace of sulphurous acid or nitrous gas, or both, escape from the chimney, while dilute sulphuric acid is being continually drawn from the chambers. The above description may be taken to fairly represent the reactions occurring during the manufacture of sulphuric acid, although there is reason to believe that the actual reactions are somewhat more complex; thus if the supply of steam is not sufficient, crystals of a compound having the composition—



are formed which decompose on addition of water into sulphuric acid, nitric acid, and nitric oxide. These "crystals of the leaden chamber," as they are called, are by some supposed to play an important part in the formation of the sulphuric acid. The acid withdrawn from the leaden chambers, technically called "chamber acid," has a specific gravity of about 1.55. It is concentrated by heat in leaden pans until it attains a specific gravity of 1.7 when it constitutes the ordinary acid of commerce, generally known as "brown acid," from its being slightly coloured by the presence of traces of organic matter. A still stronger acid is obtained by further concentration in stills of glass or platinum when a dilute sulphuric acid, contaminated with sulphurous acid, distils over, a colourless acid of specific gravity 1.84 being drawn from the still. This, with the exception of the Nordhausen, is the strongest commercial acid, and is known as oil of vitriol. This acid always contains lead as an impurity and, occasionally, arsenic. Pure sulphuric acid is a heavy, oily liquid, colourless and odourless. Its specific gravity is 1.84; it boils at 327°. It is exceedingly hygroscopic, and will gain considerably in weight from

even a short exposure to moist air, hence it is used as a desiccating agent. If mixed directly with water a great elevation of temperature ensues, and a peculiar action on many organic compounds is the abstraction of the elements of water. Sugar, and organic substances of a similar nature, are charred by strong sulphuric acid.

Sulphuric acid forms two well defined hydrates, a monohydrate,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , and a dihydrate,  $2\text{H}_2\text{O}$ . The first compound has a specific gravity 1.78, and may be solidified to a mass of crystals by exposure to a temperature of  $8^\circ$ , hence it is sometimes termed glacial sulphuric acid. It decomposes at from  $205^\circ$  to  $210^\circ$ , giving off a weak acid, and may be obtained by the concentration of a weaker acid at a temperature not exceeding  $100^\circ$ . The specific gravity of the second hydrate is 1.62, and it boils at  $338^\circ$ . Sulphuric acid is decomposed by exposure to red heat, and a process for the preparation on a large scale has been founded on this reaction. Sulphuric acid is allowed to flow on to red hot iron, when it splits up into sulphurous oxide, and oxygen; the sulphurous oxide is absorbed by water.

Sulphuric acid is dibasic, forming two classes of salts, similar to carbonic and sulphurous acids. Sulphuric acid may be regarded as hydrogen sulphate, while  $\text{KHSO}_4$  is hydrogen, potassium sulphate, and  $\text{K}_2\text{SO}_4$ —potassium sulphate, the normal compound. Sulphuric acid forms an extensive series of salts, and decomposes nitrates, chlorates, carbonates, acetates, etc., with liberation of the combined acid, and formation of a sulphate.

Sulphuric acid is largely used for the preparation of nitric and hydrochloric acids, as a solvent for metallurgical operations, and for many other purposes. Its greatest consumption is in the conversion of sodium chloride into sodium sulphate as a first step in the manufacture of sodium carbonate by Leblanc

Sulphuric acid in solution may be identified by the production of a white precipitate of Barium sulphate on addition of Barium chloride. This precipitate is insoluble in acids.

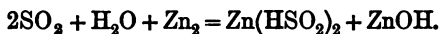
**HYPOSULPHUROUS ACID,  $H_2S_2O_3$ .**—This acid is only known in combination, the sodium compound (hyposulphite of soda) being its principal salt. This salt may be prepared by boiling sulphur with soda ley, and subsequently passing a current of sulphurous oxide until the solution is decolorised.



The crystallized salt contains five equivalents of water, and is largely used in photography for rendering the pictures permanent, an effect due to its solvent action on the unchanged silver salts. This process is technically known as 'fixing.'

A solution of a hyposulphite may be identified by the evolution of sulphurous acid, and the precipitation of sulphur on the addition of hydrochloric or sulphuric acid, and exposure to a gentle heat.

Hydrosulphurous Acid,  $H_2SO_2$ , is formed as a zinc compound when an aqueous solution of sulphurous acid is placed in contact with zinc.



The free acid may be obtained by decomposing the sodium compound with oxalic acid. It is an orange-yellow, unstable liquid, possessing reducing and bleaching properties.

The remaining compounds of sulphur and oxygen are of sufficient importance to be here noticed. The following table shows concisely the preparation and properties of the leading oxides and oxacids of sulphur:—

*Table showing the Mode of Preparation and Leading Characteristics of the Principal Oxides and Oxacide of Sulphur :—*

NAME	SYMBOL	MODE OF PREPARATION	LEADING CHARACTERISTICS
Sulphur dioxide Sulphurous oxide or Sulphurous anhydride.	SO <sub>2</sub>	By the combustion of sulphur in air or oxygen. $S + O_2 = SO_2$ By heating metallic mercury or copper with sulphuric acid. $Hg + 2H_2SO_4 = SO_2 + HgSO_4 + 2H_2O$ $Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O$	Colourless gas, having the suffocating odour of burning sulphur, condensed to a colourless liquid at $-10^\circ$ , and freezing to a transparent solid at $-76^\circ$ ; soluble in water, forming sulphurous acid, H <sub>2</sub> SO <sub>3</sub> ; possesses bleaching properties, and is a reducing agent.
Sulphur trioxide Sulphuric oxide, or Sulphuric anhydride.	SO <sub>3</sub>	By the passage of dry SO <sub>2</sub> and dry O over finely divided platinum at a red heat. $SO_2 + O = SO_3$ By the distillation of Nordhausen sulphuric acid, and by the dry distillation of bi-sulphate of soda.	White crystalline solid, melting at $16^\circ$ and boiling at $46^\circ$ , combines with water with great energy, and evolution of heat to form sulphuric acid H <sub>2</sub> SO <sub>4</sub> .

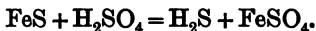
suphate.		<p>slow oxidation of <math>\text{SO}_2</math> by nitrogen trioxide in the presence of air and moisture.</p>	<p>Syrupy liquid of specific gravity 1.86, boiling at about <math>327^\circ</math>; possesses powerfully acid properties, chars organic substances; has a great affinity for water, and is used as a desiccating agent; forms an extensive series of salts with bases.</p>	
Hyposulphurous acid.	$\text{H}_2\text{S}_2\text{O}_3$	<p>Hyposulphites are formed when solutions of sulphites are boiled with sulphur.</p> $\text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3$ <p>By passing a current of <math>\text{SO}_2</math> through an alkaline solution of a sulphide.</p> $2\text{Na}_2\text{S} + 2\text{NaOH} + 4\text{SO}_2 = 3\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$	<p>Not known in the free state, but forms an important class of salts, the hyposulphites.</p>	
Hydrosulphurous acid.	$\text{H}_2\text{SO}_2$	<p>By decomposing sodium hydrosulphite with oxalic acid.</p>		<p>Yellow liquid, possessing powerful reducing properties; bleaches vegetable colouring matter; readily decomposes.</p>



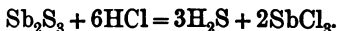
## COMPOUNDS OF SULPHUR AND HYDROGEN

These are two in number, viz., hydrogen sulphide, more commonly known as sulphuretted hydrogen,  $\text{H}_2\text{S}$ , and hydrogen disulphide,  $\text{H}_2\text{S}_2$ .

**HYDROGEN SULPHIDE,  $\text{H}_2\text{S}$ .**—This compound is best obtained by the action of dilute sulphuric acid on iron sulphide.



It may also be obtained by acting on antimony tersulphide with strong hydrochloric acid with the assistance of heat.

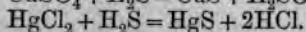
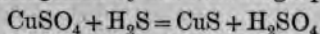


The first method is that by which sulphuretted hydrogen is always prepared in the laboratory. The gas should be passed through a small quantity of water in order to wash it, and may then be collected over warm water, or by displacement.

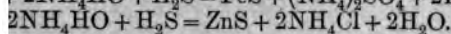
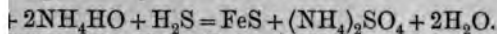
Sulphuretted hydrogen is a colourless transparent gas, having an odour of rotten eggs. It is inflammable, and burns with a bluish flame, the products of combustion being sulphurous oxide and water. It acts as a poison when inhaled. At the ordinary temperature, water dissolves about three times its own volume of sulphuretted hydrogen. The solution possesses the characteristic odour of the gas, and reddens blue litmus paper. Hydrogen sulphide may be liquefied by exposure to a temperature of  $-74^\circ$ , or at the ordinary temperature by a pressure of about seventeen atmospheres. It forms a colourless mobile liquid, which solidifies at a temperature of  $-85^\circ$ .

Hydrogen sulphide is a most useful re-agent in the laboratory for the separation of the metals, with most of which it forms characteristic insoluble sulphides. By the use of the gas, the metals are divided into groups, thus facilitating the analyses of mixed metallic solutions. A third group comprises the alkalis and

earths, which are not precipitated by sulphuretted hydrogen under any condition. The action of sulphuretted hydrogen on metals of the first group, exemplified by the following equations :—



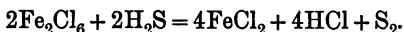
As examples of the action of the gas on the second group, we may take Iron and Zinc—



*Showing the Action of Sulphuretted Hydrogen on Metals in Solution, and their Division into Groups:—*

	NAME OF METAL	COLOUR OF SULPHIDE
GROUP I. Metals which are precipitated by sulphuretted hydrogen from acid solutions.	Lead Copper Bismuth Mercury Tin Gold Platinum Cadmium Antimony Arsenic	Black      Yellow Orange Yellow
GROUP II. Metals which are not precipitated from their solutions by sulphuretted hydrogen, but are thrown down from their neutral solutions by ammonium sulphide, and their alkaline solutions by sulphuretted hydrogen.	Iron Cobalt Nickel Manganese Zinc Chromium Aluminium	Black   Flesh-coloured White These two metals are thrown down as hydrates.

Sulphuretted hydrogen sometimes sets as a reducing agent, reducing, for instance, Ferric chloride to the ferrous state.



Sulphuretted hydrogen may be recognised by its peculiar odour, and by the formation of characteristic sulphides with many of the metals. The most delicate test for the gas consists of slips of paper moistened with a solution of lead acetate or silver nitrate which are discoloured or blackened by exceedingly minute quantities of sulphuretted hydrogen.

A calculation of the amount of sulphur in sulphuretted hydrogen will furnish an additional example of the methods by which general chemical calculations are made to those already given. Supposing, for instance, it is asked, what is the amount of sulphur in grams contained in 10 litres of the gas at 1000 mm., and 27°. Firstly reducing the volume to the standard temperature and pressure, thus—

$$\frac{10 \times 1000 \times 273}{760 \times 300} = 11.97 \text{ litres at } 0^\circ \text{ and } 760 \text{ mm.}$$

Now the density of  $\text{H}_2\text{S}$  is  $\frac{34}{2} = 17$ , and the litre weighs therefore  $.08936 \times 17 = 1.5191$  grams, and the weight of the 11.97 litres is therefore  $1.5191 \times 11.97 = 18.183$  grams. As the equivalent weight of  $\text{H}_2\text{S}$  is 34, of which 32 parts are sulphur, the amount of S in the 18.183 grams of  $\text{H}_2\text{S}$  is easily calculated—

$$34 : 18.183 :: 32 : x$$

$$x = 17.11 \text{ grams of sulphur.}$$

In the same way the sum may be worked conversely as an answer to the question. What volume of sulphuretted hydrogen at 1000 mm. and 27, is the

equivalent of 17.11 grams of sulphur. First converting the S into  $H_2S$ —

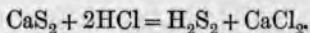
$$32 : 17.11 :: 34 : x$$

$$x = 18.18$$

Then to find the volume of  $H_2S$  in litres at the standard temperature and pressure corresponding to 18.18 grams, divide this amount by the weight of a litre— $18.18 \div 1.519 = 11.97$  litres. Finally, to find the volume this 11.97 litres, at the standard temperature and pressure, would occupy at 1000 mm. and  $27^\circ$ —

$$\frac{11.97 \times 760 \times 300}{1000 \times 273} = 9.99 = 10 \text{ litres}$$

HYDROGEN DISULPHIDE,  $H_2S_2$ , also called hydrosulphuryl, may be prepared by pouring a solution of calcium disulphide into hydrochloric acid—



It precipitates as an oily liquid, which possesses bleaching properties, and readily splits up into sulphur and sulphuretted hydrogen.

### SULPHUR and CHLORINE

Sulphur and chlorine form by direct union three compounds— $S_2Cl_2$ ,  $SCl_2$ , and  $SCl_4$ . They may be produced by passing a current of dry chlorine over melted sulphur. The disulphide  $SCl_2$  is the only compound readily obtainable in a pure state. It is a mobile liquid of a reddish yellow colour, and disagreeable odour, fuming strongly in the air. Its specific gravity is 1.68, and it boils at  $136^\circ$  to  $139^\circ$ .

## SELENIUM

SYMBOL, Se

COMBINING WEIGHT, 79.5

**DISTRIBUTION.**—Selenium was discovered by Berzelius in 1817 in the refuse from a sulphuric acid manufactory at Gripsholm in Sweden. It is not an abundant element, and is found in nature in both the free and combined condition. It occurs free at Culebras in Mexico, and combined in association with sulphur in the iron pyrites of Fahlun in Sweden, and other localities.

**PREPARATION.**—The preparation of selenium is somewhat difficult, and the method used varies with the description of ore which has to be treated. The details need not be described here, but may be obtained by reference to the larger text books.

**PROPERTIES.**—Selenium is much allied to sulphur in its properties and characteristics. It is a brittle solid of deep brown colour and glassy fracture. Like sulphur it forms several allotropic modifications.

Amorphous selenium is deposited from a solution of selenhydric acid on exposure to air, and may also be prepared by acting on aqueous selenious acid by sulphurous acid. The powder produced is in the first case soluble in carbon disulphide, and in the second case insoluble. Amorphous selenium softens by heat, becomes semi-fluid at 100°, and perfectly liquid at a slightly higher temperature. Vitreous selenium is obtained by fusion, and has a specific gravity of 4.4 to 4°, while the crystalline variety may be obtained from the spontaneous evaporation of a carbon disulphide solution. Selenium is inflammable, burning with a bright blue flame, and evolving an odour resembling that of decayed horse-radish. This odour is due to the formation of an oxide, the nature of which is at

present unknown. Selenium much resembles sulphur in its properties. It forms selenides with the metals, which on treatment with an acid evolve hydrogen selenide in the same way that sulphides yield hydrogen sulphide. It combines with oxygen as selenious oxide, with a corresponding acid, the selenious, producing salts termed selenites with bases, much resembling the sulphites in their properties, and it further forms an oxacid, the selenic which forms selenates with bases, corresponding with sulphates, with which they are, indeed, isomorphous.

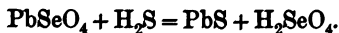
#### COMPOUNDS OF SELENIUM AND OXYGEN

SELENIUM DIOXIDE,  $\text{SO}_2$ , is formed when selenium is burnt in air or oxygen, and also by the action of nitric acid or aqua regia. It is a white crystalline substance, soluble in water, with formation of selenious acid.

SELENIUS ACID,  $\text{H}_2\text{SeO}_3$ , is produced as above, is dibasic, forms selenites with bases, and deposits amorphous selenium when treated with sulphurous acid.



SELENIC ACID,  $\text{H}_2\text{SeO}_4$ , is obtained by fusing selenium or a selenite with potassium nitrate. The fused mass is dissolved in water, and a lead salt added, when insoluble selenide of lead is precipitated, which, on treatment with hydrogen sulphide, yields lead sulphide and selenic acid—



The dilute acid so obtained is concentrated in the water bath, when it forms a transparent colourless liquid of specific gravity 2.6, and boiling at  $280^\circ$ . It cannot, however, be heated to this temperature without being more or less decomposed into selenium dioxide,

oxygen, and water. Selenic acid is dibasic, and forms salts termed selenates.

### SELENIUM AND HYDROGEN

Seleniuretted hydrogen, or hydrogen selenide,  $\text{HSe}$ , is obtained by the action of an acid on a selenide. It is a colourless inflammable gas, of a disagreeable odour.

## TELLURIUM

SYMBOL,  $\text{Te}$

COMBINING WEIGHT, 129

**DISTRIBUTION.**—Tellurium is a very rare element only found in a few localities, chiefly in Hungary and Transylvania. It occurs in nature in a comparatively pure condition, but its principal ores are those of bismuth, lead, gold, and silver.

**PROPERTIES.**—Tellurium is a tin-white, shining, brittle metal, having a tendency to crystallisation, the crystals belonging to the hexagonal system. Its specific gravity is from 6.1 to 6.3, and it melts at about  $500^{\circ}$ . Although so much resembling a metal in its physical appearances, tellurium is more closely allied to sulphur and selenium in its chemical properties. Thus it forms compounds with the metals called tellurides, resembling sulphides and selenides, and evolving a hydrogen compound,  $\text{H}_2\text{Te}$ , on treatment with an acid. It also forms compounds with oxygen, tellurous oxide,  $\text{TeO}_2$ , and telluric oxide,  $\text{TeO}_3$ , with the corresponding oxacids which are dibasic, and which, with bases, yield tellurites and tellurates resembling the corresponding sulphur and selenium compounds.

## CARBON

SYMBOL, C

COMBINING WEIGHT, 12

**DISTRIBUTION.**—Carbon, in one condition or another, has been known from the earliest periods. It occurs in nature in a pure form, as the diamond, and in a less pure condition, as graphite. It also forms the greater bulk of anthracite and the different varieties of coals and lignites, as well as of the various organic structures of animal and vegetable life. Coke and charcoal also consist almost entirely of carbon. In the gaseous condition carbon is found in the atmosphere as carbonic acid, where it plays an important part in the growth and maintenance of plant life, and in the form of carbonic acid, carbon likewise forms a large constituent of limestone rocks.

**PREPARATION.**—Coke, charcoal, and lampblack are examples of artificially prepared carbon. Coke is prepared by exposing any variety of coal to a red-heat in closed vessels of iron or fireclay. The greater part of the coke of commerce is produced during the manufacture of coal gas, but specially dense varieties are made for special purposes by the carbonisation of coal in coke ovens, where by a long exposure to a high temperature the coke is made of greater density and more difficult of combustion. Charcoal is produced either by the slow combustion of heaps of wood covered with turf, the combustion being stopped when the thorough carbonisation of the wood has been effected, or, more economically by exposing wood to a red-heat in closed retorts, when the bye-products, tar, pyroligneous acid, and wood naphtha are collected and utilised. Lampblack is prepared from the imperfect combustion of oil, resin, or tar. Any one of these substances is burnt with a limited supply of air, which results in the production of a quantity of finely divided carbon



in the form of soot. The products of combustion are conducted to a series of chambers, where the lampblack is deposited according to its degree of fineness, the most impalpable material, which is commercially the most valuable, being deposited at the greatest distance from the seat of combustion.

**PROPERTIES.**—Carbon exists in three different forms, termed allotropic modifications, viz., crystalline, as the diamond; graphoidal, as graphite; and amorphous, as coke, charcoal, lampblack, etc. The crystalline form of carbon, the diamond, is found in India, Borneo, Brazil, the Urals, and South Africa, in some alluvial soils produced by the disintegration of ancient rocks. Diamonds are of many colours, the purest being colourless and transparent, the less pure specimens ranging through a variety of shades, from yellow, red, and green to brown and black. The diamond crystallises in the regular system (octahedral), and has a specific gravity of 3.5. Exposed to a high temperature in air or in oxygen, it burns to carbonic anhydride, leaving only a trace to ash.

**GRAPHITE** is found in a native state at Borrowdale in Cumberland, Griesbach in Germany, and other places. As usually met with it is an opaque substance, having an iron-black or steel-grey colour and metallic lustre, and leaving a black shikey streak on paper. It contains from 95 to 100 per cent. of carbon, the impurities consisting of iron, with a little silica and alumina. The specific gravity is 1.20. Two varieties of graphite are known, the foliated and the amorphous; the former variety is sometimes produced artificially during the fusion of cast iron containing much carbon. The amorphous variety of graphite is more commonly termed "plumbago," or "black lead."

Graphite may be separated from the earthy impurities which it contains, and rendered pure by treatment with potassium chlorate and strong sulphuric acid. By treating powdered graphite with a mixture of sulphuric

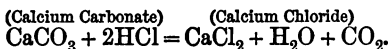
and nitric acids, washing the product with water, and repeating the treatment several times, a peculiar substance is obtained in thin transparent crystals to which the name graphitic acid has been given, and which has the formula  $C_{11}H_4O_5$ . Graphite is used for lead pencils, for polishing the surface of iron work, etc., and for imparting a polish to gunpowder. Of the amorphous varieties of carbon there are a great number, of which the principal ones, such as charcoal, lamp-black, etc., have been already mentioned. Charcoal is produced whenever organic substances are exposed to a red-heat in closed vessels, and the freer the organic substance is from earthy and saline impurities, the purer is the resulting charcoal. Besides wood charcoal used principally as fuel, animal charcoal is prepared on an extensive scale by the carbonisation of animal substances, bones being the chief material used. The product obtained is called bone black. Ivory black is produced by treating ivory in a similar way, and is used in the preparation of the finer sorts of printer's ink for engraving. Bone black is most extensively used for sugar refining. It possesses the property of absorbing vegetable colouring matters from solution, and so acting as a decolorising agent. All varieties of charcoal possess the property of removing the organic colouring matters, as well as of destroying the odour of putrefying vegetable and animal substances, but bone black possesses these properties in the highest degree. Ordinary wood charcoal is a combustible and most unchangeable substance, which possesses the singular property of condensing many gases in its pores. It has been found to absorb 90 times its volume of gaseous ammonia, 55 of sulphuretted hydrogen, 35 of carbonic anhydride, and  $9\frac{1}{4}$  of oxygen. It is owing to this absorbent property that charcoal acts as a powerful deodoriser. Foul gases are absorbed, and by being brought into intimate contact with oxygen in the pores of the material, become rapidly oxidised. By this means foul

water may be purified by filtration through powdered charcoal. The organic impurities are absorbed and oxidised, the carbon and hydrogen forming carbonic acid and water, and the nitrogen passing into the form of ammonia, and of nitrous and nitric acids. Powdered charcoal also possesses a power of absorption apart from oxidation and by which several definite organic compounds, such as the vegito-alkaloids, may be abstracted from their aqueous solution, and subsequently obtained unchanged by treating the charcoal with an appropriate solvent. The presence of carbon in any substance may be recognised by the blackening produced on the application of heat, and by the identification of carbonic acid among the products of combustion.

#### COMPOUNDS OF CARBON AND OXYGEN

These are two in number, viz., carbonic anhydride or carbon dioxide, commonly called carbonic acid,  $\text{CO}_2$ , and carbonic oxide,  $\text{CO}$ .

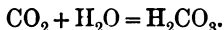
Carbon dioxide,  $\text{CO}_2$ , is found in small quantity in the atmosphere and in natural waters. It is evolved from volcanoes, and occurs in the products of respiration. It is also given off by fermenting liquids, and from the combustion of fuels and the decay of organic substances. It constitutes the so-called "choke damp" of the miner. Carbon dioxide is best prepared by acting on fragments of chalk or marble with dilute hydrochloric acid, thus:—



In the preparation, hydrochloric acid is used instead of sulphuric acid, as the latter forms an insoluble sulphate of lime, and protects the material from the further action of the acid. Any carbonate may be made to yield carbon dioxide by treatment with one of the stronger acids. Carbon dioxide may also be prepared

by the combustion of charcoal in oxygen. It is a colourless gas, possessing a slightly acid taste and smell, and soluble in its own volume of water at ordinary temperatures and pressures. At either a lower temperature or greater pressure, a larger volume of the gas is absorbed. The increased amount of the gas which an aqueous liquid can retain under increased pressure, is well illustrated in the case of the so-called effervescent waters, or of champagne, a bottle of which when opened allows a large quantity of carbon dioxide to escape from the sudden reduction of pressure. The brisk taste of these liquids, as well as that of many spring and deep well waters, is mainly due to dissolved carbon dioxide. Exposed to a pressure of 36 atmospheres, and a temperature of  $0^{\circ}\text{C}$ ., carbon dioxide is condensed to a colourless liquid. If this liquid is allowed to escape into the air in the form of a fine jet, such rapid evaporation ensues that a portion of the carbonic anhydride is frozen, and may be collected in the form of a fine white snow. In the liquefaction of carbon dioxide, as well as of liquefiable gases generally, the reduction to the liquid form cannot be accomplished by pressure alone, a certain temperature being necessary, above which, however the pressure may be increased, the gas still maintains its gaseous condition. Each liquefiable gas has its particular temperature, called "*the critical point*," above which liquefaction cannot be effected. In carbon dioxide this critical temperature is  $31^{\circ}$ .

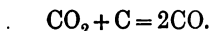
Carbon dioxide is a non-supporter of combustion and of animal life. It unites with water to form carbonic acid.



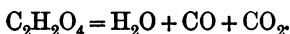
The acid has not been isolated in a free state. It is dibasic and its salts are known as carbonates.

CARBON MONOXIDE, or carbonic oxide ( $\text{CO}$ ), is formed when carbon is burnt with a limited supply of oxygen

or where carbon dioxide meets with an excess of carbon at a red heat. The last named mode of formation is frequently observed in a fire of coke or charcoal, where the carbon dioxide, formed at first from the complete combustion of the lower part of the fuel, is reduced to carbonic oxide in passing upward through the incandescent carbon, and is finally observed burning with a blue lambent flame at the top of the fire.



Carbonic oxide may be prepared by passing a slow current of oxygen or carbon dioxide through a tube containing fragments of charcoal heated to redness. A better mode of preparation, however, and one by which a purer product may be obtained, consists in heating oxalic acid with strong sulphuric acid. The sulphuric acid withdraws the elements of one molecule of water, leaving the compound,  $\text{C}_2\text{O}_3$ , which cannot exist in the free state, but immediately splits up into  $\text{CO}$  and  $\text{CO}_2$ , thus :—



The carbon dioxide may be removed by passing the two gases through a solution of caustic potash, when carbon dioxide is absorbed, and pure carbonic oxide passes on and may be collected.

Carbon monoxide is a colourless gas possessing neither taste nor smell. It is very slightly soluble in water. It is a most powerful poison, the inhalation of comparatively small quantities causing death; the fatal effects of the fumes from charcoal fires and lime kilns are mainly due to the carbon monoxide present. In cases of death resulting from breathing carbonic oxide the blood is found of a remarkably red colour. Butcher's meat placed in this gas, or in ordinary coal gas, which contains it, maintains its ruddy colour for some days. Carbonic oxide is removed from gaseous mixtures which contain it by treatment with an acid solution of

cuprous chloride, which has the property of absorbing it. The compounds of carbon with chlorine, hydrogen, nitrogen, and sulphur, will be described under "Organic Chemistry."

## COAL GAS

Although the compounds of carbon and hydrogen come more within the province of organic chemistry, it will be advisable in this place to consider shortly the manufacture of the coal gas so extensively used for lighting and heating purposes. Coal contains as its constituent elements carbon and hydrogen, with smaller quantities of nitrogen and sulphur, and a small but variable quantity of mineral matter. In the manufacture of coal gas, coals are selected which contain a large quantity of hydrogen, a class more known as bituminous coals. These are placed in large fire-clay retorts, and subjected to a cherry-red heat. The coal becomes decomposed, gaseous compounds of carbon and hydrogen, together with free hydrogen and more or less solid and liquid hydro-carbons being evolved, while the excess of carbon remains behind in the retort as coke. The crude gas, which, in addition to the substances already named, contains ammonia, sulphuretted hydrogen, and carbonic acid, passes through a series of iron pipes, called condensers, in which the solid and liquid hydro-carbons are separated, and condense as tar. From the condensers the gas passes to large vessels filled with coke, which is kept in a wet condition by a stream of water, by which the ammonia is removed, together with some sulphuretted hydrogen and carbonic acid; the weak solution of ammoniacal salts thus formed is known as "gas liquor," and is the principal source of the ammonia of commerce. The partially purified gas then passes to large vessels charged with lime and oxide of iron, called purifiers, where the remaining sulphuretted hydrogen and carbonic acid are removed, and the puri-

fied gas is then stored in holders for use. The average composition of the purified gas is as follows:—

DESCRIPTION	Hydrogen	Marsh Gas, $\text{CH}_4$	Hydro-Carbons other than Marsh Gas	Carbonic Oxide	Aqueous Vapour	Nitrogen, Oxygen and Carbonic Acid
Gas from Common Coal	46.0	39.5	3.8	7.5	2.0	1.2
Gas from Cannel Coal	27.7	50.0	13.0	6.8	2.0	0.5

The common and cannel gas mentioned in the above table are procured—the first from ordinary gas coals, and the second from a special variety of coal which yields more luminous gas. The common gas supplied to London is required to have an illuminating power equal to 16 sperm candles, each burning 120 grs. per hour, the gas being consumed in a special burner at the rate of five cubic feet per hour. The cannel gas is required to have an illuminating power equal to twenty candles.

The following are the chief solid and liquid products obtained from the destructive distillation of coal, and which are all present to a greater or lesser extent in coal tar :—

Neutral Hydro-carbons	Solid	Naphthaline	$\text{C}_{10}\text{H}_8$
		Anthracene	$\text{C}_{14}\text{H}_{10}$
		Chrysene	$\text{C}_{18}\text{H}_{12}$
		Pyrene	$\text{C}_{16}\text{H}_{10}$
	Liquid	Benzole	$\text{C}_6\text{H}_6$
		Toluole	$\text{C}_7\text{H}_8$
		Xylol	$\text{C}_8\text{H}_{10}$
		Cumole	$\text{C}_9\text{H}_{12}$
Alkaline Products		Ammonia	$\text{NH}_3$
		Aniline	$\text{C}_6\text{H}_7\text{N}$
		Picoline	$\text{C}_6\text{H}_7\text{N}$
		Quinoline	$\text{C}_8\text{H}_7\text{N}$
		Pyridine	$\text{C}_5\text{H}_5\text{N}$

Acids	{	Carbolic Acid (Phend)	$C_6H_6O$
		Kresylic Acid	$C_7H_8O$
		Rosolic Acid	$C_{22}H_{22}O_4$
		Brunolic Acid	
		Acetic Acid	$C_2H_4O_2$

**STRUCTURE OF FLAME.**—Flame may be defined as consisting of gas in a high state of ignition. In the case of the combustion of an inflammable gas, the above definition is obvious, but in the case of the combustion of a candle the analogy is, at the first glance, not so easily perceived. In the latter case, however, the solid constituents of the candle are first liquefied by heat, and the liquid then ascends the wick by capillary attraction, and coming into the zone of combustion, is first converted into the gaseous condition, and finally consumed. If we examine the flame of a candle, we can see that it consists of three distinct portions, *firstly*, a dark space surrounding the wick, which consists of unburnt gas; *secondly*, a luminous area of incomplete combustion; and *externally*, an area of complete combustion. The fact of the existence of gaseous matter in the dark central zone of a flame may be proved by the introduction of a small piece of glass tubing, when a portion of the unburnt gases will pass up the tube, and may be ignited at the opposite extremity. Flames may be divided into Luminous and Non-luminous. Luminous flames are generally produced by the combustion of bodies rich in carbon, and their light-giving power is explained by the fact that in the combustion of the hydro-carbon in the middle zone of the flame, where there is a comparatively limited supply of air, the hydrogen is first consumed, the carbon being liberated in the solid form, and heated to a degree sufficient to evolve light. The carbon particles subsequently pass to the outermost zone of the flame, where there is a plentiful supply of oxygen, and are consumed, carbonic acid being formed. In the flame of a hydro-carbon, which, like marsh gas, contains but little carbon, the



carbon and hydrogen are both immediately consumed, forming carbonic acid and water, and no light is evolved. That light is evolved from the incandescence of a solid body, is shown in the lime-light and in the electric light; the luminosity being due to the incandescence of solid lime in the first case, and solid carbon in the second. In the combustion of a substance such as coal gas, which gives in ordinary cases a luminous flame, the admixture of sufficient oxygen to directly consume the hydrogen and carbon, destroys the luminosity. This is exemplified in the well known Bunsen or atmospheric gas burner. In the blow-pipe flame, the internal zone of combustion, where there is a deficient air supply, possesses reducing properties from the fact of its readily abstracting oxygen from substances submitted to its action. The external portion of the flame, where the air is in excess, possesses, on the other hand, great oxidising power. Every mixture of gas requires a certain temperature to inflame it, a principle which is utilised in the well-known Davy lamp. If a piece of wire gauze, containing about 700 meshes to the square inch, is held over a gas burner from which gas is issuing, and the gas above the gauze is ignited, the gauze may be lifted some distance above the burner, carrying the flame with it. In this case the metal of the gauze conducts away the heat so quickly that the inflammable gas beneath never reaches a sufficient temperature to become ignited. In the Davy lamp, which consists simply of an ordinary oil lamp surrounded completely with wire gauze, the air necessary for combustion passes freely through the meshes, but an inflammable gas cannot be ignited from the flame of the lamp owing to the heat-conducting power of the surrounding casing.

## SILICON

SYMBOL, Si

COMBINING WEIGHT, 28

DISTRIBUTION.—Silicon is a very widely diffused

element, ranking next to oxygen in its abundance, but it is never met with in the free state, nearly always occurring in union with oxygen, as silica, which is found as flint, sand, quartz, and rock crystal, and in a variety of minerals. In union with oxygen, silicon also occurs in nature combined with metals, as silicates.

**PREPARATION.**—Silicon is best obtained by heating potassium silico-fluoride with metallic potassium.



Potassium silico-fluoride and metallic potassium forming silicon and fluoride of potassium. The reaction takes place with considerable violence, and on treatment of the product with water, silicon remains as a brown amorphous powder.

**PROPERTIES.**—Silicon, like carbon and boron, exists in three allotropic modifications, viz., the amorphous, the graphitoidal, and the crystalline. Amorphous silicon, the preparation of which has been already described, is a brown powder, insoluble in water, and not acted on by nitric or sulphurous acids. It burns brilliantly in the air when heated, forming silica. Graphitoidal silicon may be obtained by exposing a mixture of aluminium and a large excess of silico-fluoride of potassium to a high temperature in a Hessian crucible, a fused button of metallic aluminium being obtained, which, on treatment with hydrochloric and hydrofluoric acid successively, leaves the graphitoidal silicon in hexagonal tablets. It may be heated to whiteness in oxygen without undergoing combustion. Crystalline silicon may be obtained by fusing a mixture of potassic silico-fluoride, sodium, and zinc. The fused mass is allowed to cool slowly, and the zinc containing the crystals of silicon dissolved by treatment with an acid. The crystals so obtained are octahedral, and are sufficiently hard to scratch glass.

Silicon forms compounds with oxygen, fluorine, chlorine, and hydrogen.

**SILICON dioxide**—silicic anhydride, silica,  $\text{SiO}_2$ . This compound has been already alluded to as very abundant in nature. It is found almost pure as rock crystal, and the colourless varieties of quartz, in which form it has a specific gravity of 2.6. The crystals occur in six-sided prisms, and are so hard as to scratch glass. Coloured with various metallic oxides, silica occurs as various precious stones, such as onyx, opal, jasper, agate, carnelian, and bloodstone, while metallic silicates are very widely distributed, and constitute a large class of minerals. Silica also exists as a constituent of plants, more especially of grasses and cereals, to the stems of which it gives rigidity. Ordinary silica is quite insoluble in water, and is not attacked by any acid, except the hydrofluoric, by the action of which silicon tetrafluoride and water are produced. Pure silica may be prepared in an amorphous condition by exposing silicic acid to heat :—



Silicic acid may be prepared by fusing clean white sand with an excess of carbonate of soda. The silica unites with the sodium of the sodium carbonate, carbonic acid being expelled, and sodium silicate or soluble glass formed. The mass is treated with water and filtered : the addition of hydrochloric acid in slight excess to the clear solution throws down the greater part of the silica acid as a gelatinous semi-transparent precipitate. Part of the silicic acid remains in solution, and may be freed from the salts and excess of hydrochloric acid by a process called "dialysis." The solution is placed in a flat vessel, the bottom of which is made of parchment paper. The vessel is then floated for several days on a considerable quantity of water, when the sodium chloride and hydrochloric acid pass through the paper, a solution of silicic acid remaining behind. This solution is concentrated by boiling until it contains about 14 per cent. of silica. The liquid so obtained is

tasteless, transparent, and colourless, and has a faintly acid reaction. It cannot be preserved for any length of time, as the silica acid separates out as a gelatinous mass. The gelatinous silica thrown down from solutions of alkaline silicates by the addition of an acid, as well as that which separates spontaneously from the dialysed solution, is a true hydrate, having the composition  $\text{SiO}_2\text{H}_2\text{O}$ . It is easily soluble in solutions of alkalis, and, to a slight extent, in solutions of alkaline carbonates, and also to a very small degree in water and acids. The silica found in some mineral waters is no doubt brought into solution in the water by the action of an alkaline carbonate, aided in some cases by heat. Gelatinous silicic acid, after drying and igniting, becomes a light white powder, which cannot be brought into solution again without fusion with an alkali or alkaline carbonate.

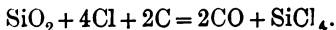
Silicates are largely used in the arts for the preparation of glass, earthenware, and cements.

#### SILICON AND HYDROGEN

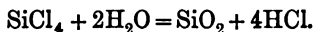
Hydrogen silicide, siliciuretted hydrogen,  $\text{SiH}_4$ , is prepared by acting on magnesium silicide with hydrochloric acid. It is a gas which takes fire spontaneously on contact with air, forming silicon dioxide and water.

#### SILICON AND CHLORINE

SILICON TETRACHLORIDE, SILICIC CHLORIDE,  $\text{SiCl}_4$ , is formed when silicon is burned in chlorine, but is best prepared by passing a current of dry chlorine over an intimate mixture of finely divided silica and carbon heated to redness. Silica alone does not unite with chlorine, but in the presence of carbon, the oxygen of the silica forms carbonic oxide with the carbon, while the silicon unites with the chlorine, thus:—



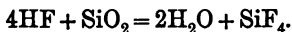
The silicon tetrachloride formed must be condensed by the use of a freezing mixture. It is a colourless, transparent liquid of specific gravity 1.52 at 0° C., and boiling at 50°. The vapour has a suffocating odour, and reddens blue litmus paper. Silicic chloride is instantly decomposed by water, forming silicic and hydrochloric acids.



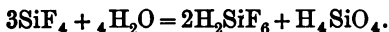
The compounds  $\text{Si}_2\text{Cl}_2$  and  $\text{Si}_2\text{Cl}_6$  are also known as well as several oxychlorides.

#### SILICON AND FLUORINE

SILICON TETRAFLUORIDE,  $\text{SiF}_4$ , is formed whenever hydrofluoric acid comes in contact with silica. It may conveniently be prepared by heating a mixture of fine sand or powdered glass with fluor spar, also powdered, and strong sulphuric acid. Hydrofluoric acid is first liberated by the action of the sulphuric acid on the calcium fluoride, and this immediately reacts on the silica with formation of silicon tetrafluoride, thus :—



The corrosive action exercised by hydrofluoric acid on glass is due to the formation of this substance. Silicon tetrafluoride is a colourless and transparent gas of pungent odour, and fuming strongly in the air like hydrochloric acid. It is decomposed by water, silica being separated and a fresh compound called silicofluoric acid or hydro-fluo-silicic acid,  $\text{H}_2\text{SiF}_6$ , is formed.



This acid, the hydro-fluo-silicic, is remarkable for forming an insoluble compound with potassium.

Fig. 6 shows the arrangement of apparatus for the preparation of hydro-fluo-silicic acid by the decomposition of silicon tetrafluoride by water.

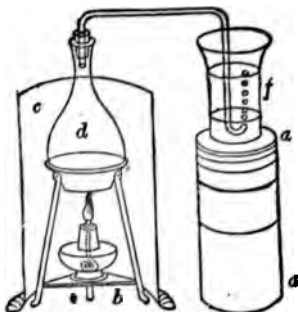


Fig 6

## GLASS

The different varieties of glass contain silica as their principal ingredient. It is curious that while the silicates of the alkalies are soluble in water, and those of the alkaline earths, although insoluble in water, dissolve in acids, that compounds of the two classes of silicates are insoluble in either water or acids. Four varieties of glass are used in the arts, viz., crown, window, or plate glass, which is a mixture of the silicates of calcium and sodium; flint glass or crystal, consisting of the silicates of potassium and lead; common green bottle glass, composed of the silicates of sodium, calcium, aluminium, and iron; and Bohemian glass not made in England, consisting of the silicates of calcium and potassium. The first two of these kinds of glass are easily fusible, ordinary bottle glass is less so, and Bohemian glass is comparatively infusible. The last mentioned glass is that mostly used for the

construction of chemical apparatus, and is in considerable demand for combustion tubing for organic analysis, and for the general construction of such laboratory apparatus as is needed to withstand a comparatively high temperature. Most of the articles for domestic use are made of flint glass.

In the manufacture of glass on a large scale, the silica is supplied in the form of white sand, the soda as "soda ash," potash as "pearl ash," the calcium is introduced as quicklime, and the lead in the form of red lead; in addition small quantities of manganese dioxide and arsenious acid are sometimes used, which improve the colour of the glass. The greatest care has to be exercised in procuring pure materials where it is desired to produce a colourless glass. The materials are fused together in pots of fire clay, and a certain proportion of broken fragments of glass called "cullet" is always added to the other substances used. Glass articles have to be very slowly cooled down after manufacture, a process called annealing, as they would otherwise be brittle and unable to stand irregularities of temperature without cracking. Coloured glasses are produced by the introduction of various metallic oxides, cobalt oxide gives blue, copper suboxide, ruby red, ferrous oxide deep green, ferric oxide yellow, oxides of manganese purple. The materials used in glass making generally contain sufficient iron to impart a light green tint to the glass, and by the addition of sufficient manganese dioxide to produce a faint violet: the colours neutralise each other, and an almost colourless glass is the result. Arsenious acid acts by oxidising any organic matter present, and by reducing ferric oxide to ferrous.

The following table gives the composition of the ordinary descriptions of glass :—

	Flint Glass	Crown Glass	Green Bottle Glass	Bohemian Glass
Silica ... ..	51·93	72·0	60·4	76·0
Lime ... ..	...	6·4	22·3	8·0
Potassium oxide	13·77	...	} 3·3	15·0
Sodium oxide ...	...	17·0		...
Lead oxide ...	33·28	...	...	...
Manganese oxide	...	} 1·0	4·0	...
Iron oxide ...	...		...	...
Alumina ... ..	...	2·6	10·4	1·0
	<hr/> 98·98	<hr/> 99·0	<hr/> 100·3	<hr/> 100·0

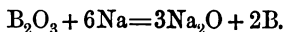
## BORON

## SYMBOL, B

## COMBINING WEIGHT, 11

**DISTRIBUTION.**—Boron is never met with in nature in the free state, but is usually found in combination with oxygen and sodium as borax or “tincal,” and also as boracic acid. Borax is imported principally from Thibet and the coast of California, while boracic acid occurs chiefly in lagoons surrounding jets of steam and gas which escape from certain old volcanic districts in Tuscany.

**PREPARATION.**—Ordinary amorphous boron may be obtained by fusing boron trioxide with sodium, or by heating the double fluoride of boron and potassium with metallic potassium :—



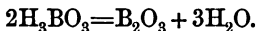
Crystalline boron is prepared by heating boron trioxide with aluminium, or by heating the amorphous form of boron with aluminium, in which case the boron is dissolved by the fused metal, and separates in crystals on cooling.



**PROPERTIES.**—Boron, as has been already stated, has its allotropic modifications, in this respect resembling carbon and silicon. Amorphous boron is a dull greenish brown or grey powder. It burns in the air when heated, producing boron trioxide, and is readily acted on by chlorine, nitric acid, and by alkalis in a fused condition. Crystalline boron occurs in square octahedrons, generally of a faint brownish colour, sufficiently hard to scratch the ruby, and with a specific gravity of 2.68. Boron is one of the few elements that unite directly with nitrogen.

#### BORON AND OXYGEN

**BORON TRIOXIDE**, boric oxide, boric anhydride,  $B_2O_3$ . This is the only oxide of boron. It is best prepared by fusing boracic acid at a red heat :—



It is a glassy looking substance, which dissolves in water to form boric acid.

**BORACIC ACID**, boric acid,  $H_3BO_3$ , is best prepared by decomposing a hot solution of borax with sulphuric acid :—



The boric acid crystallises out in white translucent six-sided laminae, which are not very soluble in cold water, but dissolve more freely with the aid of heat. It is more soluble in alcohol, and the solution burns with a beautiful green flame. Boric acid unites with bases to form borates, of which two distinct kinds are recognised, viz., neutral salts containing equivalent proportions of base, and acid, and the so-called acid salts. Borates are also sometimes classified into ortho, and meta-borates, so-called from the analogy of the compounds to the ortho and meta-phosphates. Ordinary borax,  $Na_2B_4O_7 = 2NaBO_2B_2O_3$ , is regarded as an acid

meta-borate, the neutral meta-borate being  $\text{NaBO}_2$ , while the basic or ortho borate is  $\text{Na}_3\text{BO}_3$ . Many metallic oxides are soluble in fused boric acid and borax, giving clear glasses of characteristic colours, hence these substances are used as re-agents in blow-pipe analyses. Boron unites with chlorine to form a trichloride,  $\text{BCl}_3$ , and with fluorine to form a trifluoride,  $\text{BF}_3$ . There is also a borofluoride and hydrofluoboric acid,  $\text{HBF}_4$ . All these compounds bear a considerable resemblance to the corresponding compounds of silicon, and are prepared in a similar way. The following table shows the leading characteristics of the three elements, carbon, silicon, and boron.

(TABLE

*Table showing the Leading Characteristics of the three elements Carbon, Silicon, and Boron :—*

NAME	SYMBOL	LEADING CHARACTERISTICS
Carbon	C	Carbon exists in three allotropic modifications, viz., crystalline, as the diamond, graphitoid, as graphite, and amorphous, as charcoal, lamp-black, coke, etc. Crystalline carbon has a specific gravity of 3.5. Graphitoid carbon is an opaque steel grey solid of specific gravity 1.2. The amorphous form varies in appearance and density. In the condition of animal charcoal and wood charcoal it is characterised by great antiseptic and deodorising properties. All the forms of carbon are, more or less, combustible, and form $\text{CO}_2$ when burnt.
Silicon	Si	Exists like carbon in the three allotropic modifications of the crystalline, graphitoid, and amorphous. Unites with oxygen, fluorine, chlorine, and hydrogen. Amorphous silicon is a brown insoluble powder, which is unattacked by nitric or sulphuric acid, and which burns brilliantly when heated in the air, forming silica $\text{SiO}_2$ .
Boron	B	Boron exists in two allotropic modifications, viz., crystalline and amorphous. The crystalline variety forms colourless octahedra of specific gravity 2.68. Amorphous boron is a dull greenish brown or grey powder, which burns when heated in the air, forming $\text{B}_2\text{O}_3$ . It is readily attacked by chlorine, nitric acid, and fused alkalis. Boron is one of the few elements that unite directly with nitrogen.

## PHOSPHORUS

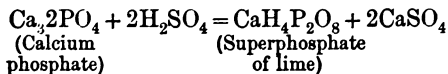
SYMBOL, P

COMBINING WEIGHT, 31

Discovered by Brandt in 1669. Scheele subsequently pointed out its existence in bones, and investigated its properties. It derives its name from  $\phi\omega\varsigma$ , light,  $\phi\epsilon\rho\omega$ , to bear.

**DISTRIBUTION.**—Phosphorus is a widely-diffused element, but is never met with in the uncombined state. Its principal native compound is calcium phosphate, found as apatite, and forming the basis of coprolites. Phosphorus, in the combined state, is an element of most fertile soils, which almost invariably contain it in small but varying quantity, derived from the disintegration of the older granite rocks. From the soil it is taken up by plants, and is by them stored principally in the seed. Through the agency of vegetable life, phosphorus finds its way into the animal organism, where it forms a large proportion of bone, and occurs in smaller quantity in the tissues and blood. It is also constantly excreted from the animal system, the urine containing it in the largest proportion.

**PREPARATION.**—Phosphorus is prepared almost exclusively from bone-ash, which consists mainly of calcium phosphate. The bone-ash is first treated with dilute sulphuric acid, which decomposes the greater part of the calcium phosphate, producing insoluble sulphate of lime, and leaving phosphoric acid in solution, in combination with a small quantity of lime, as a compound known as superphosphate of lime. The action may be represented thus :—

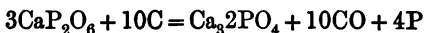


The insoluble sulphate of lime is strained off, and the solution of superphosphate of lime evaporated to a

syrup, mixed with powdered charcoal, and evaporated to dryness. The superphosphate of lime then loses water, and becomes metaphosphate of lime, thus :—



The dry mass is then heated to bright redness in fire-clay retorts, the extremities of whose necks dip beneath the surface of water. The following action then occurs :—



The phosphorus distils over and falls to the bottom of the water in yellow drops, while ordinary bone phosphate is left in the retorts, together with the excess of charcoal. The crude phosphorus is purified by melting under hot water, and straining through chamois leather or layers of charcoal, or by re-distillation. Purification is also effected by treating the crude material with potassium chromate and sulphuric acid.

PROPERTIES.—Phosphorus at ordinary temperatures much resembles imperfectly bleached wax in appearance and consistency, but when the temperature is lowered it becomes brittle. It has a specific gravity of 1·8, melts at 44° to a transparent liquid, and boils at 290°. In the air phosphorus evolves an odour of garlic, and suffers a slow oxidation, emitting white fumes of phosphorus trioxide,  $\text{P}_2\text{O}_3$ . This oxidation is attended with the emission of a pale phosphorescent light, which may be seen in the dark. Phosphorus is poisonous, and is also exceedingly inflammable; it may be ignited by being raised to its fusing point, by slight friction, or by a blow; even the warmth of the hand has been known to cause its ignition, and the greatest care should be exercised in handling it, any cutting or breaking required being conducted under water. The combustion of phosphorus in air is attended with the evolution of a brilliant light, and the emission of white fumes of the pentoxide,  $\text{P}_2\text{O}_5$ . Phosphorus is insoluble

in water, alcohol, or ether, but dissolves freely in carbon disulphide, and to a less extent in oils. Hence oil should not be given in cases of poisoning by this substance. An allotropic modification of phosphorus is obtained by heating the ordinary variety to a temperature of about  $240^{\circ}$  for about fifty hours in an atmosphere incapable of chemical action upon it, such as nitrogen or carbonic anhydride. No alteration in weight occurs, but a substance is produced totally differing from ordinary phosphorus in its physical, and to a certain extent in its chemical, properties. It is red, opaque, insoluble in carbon disulphide, infusible, not inflammable, and not poisonous. It is converted into the ordinary variety by exposure to a temperature of  $260^{\circ}$ .

The principal use of phosphorus is for the preparation of lucifer matches, but for this purpose the red amorphous variety is gradually replacing the ordinary kind, a substitution the more desirable from the non-poisonous nature of the latter substance, and from its not giving rise to the distressing disease of the jaw, which ordinary phosphorus occasions in those who work with it.

Free phosphorus may be recognised, even in the most minute quantity, by its peculiar and characteristic odour, and by its luminosity in the dark. When mixed with other substances, its presence may be detected by adding to the suspected substance dilute sulphuric acid, in order to neutralise any ammonia present, and then distilling the mixture in a glass retort fitted with a long condensing tube passing into a receiver. The distillation must be conducted in the dark, when the luminosity of the phosphorus betrays its presence.

In the combustion of phosphorus, two equivalents of that substance—viz.,  $31 \times 2 = 62$ —combine with five equivalents  $= 16 \times 5 = 80$ , of oxygen, to form 142 parts of  $P_2O_5$ . We can thus calculate the quantity of

oxygen required for the complete combustion of any named quantity of phosphorus. Say, for instance, it is required to ascertain what volume of oxygen at  $15^{\circ}$  and 1000 mm. is required for the complete combustion of 10 grams of P. Firstly, to find the required *weight* of oxygen :—

$$\begin{array}{ccccccc} 62 & : & 10 & :: & 80 & : & x \\ & & & & x = 12.90 \end{array}$$

Then, to find the equivalent volume :—As 1.4297 gram of O measures one litre, the equivalent of the 12.9 grams is  $12.9 \div 1.4297 = 9.023$ .

This 9.023 litres is the required volume at the standard temperature and pressure, which must now be corrected to the temperature and pressure required, viz.,  $15^{\circ}$  C. and 1000 mm. :—

$$\frac{9.023 \times 288 \times 760}{273 \times 1000} = 7.23 \text{ litres, Ans.}$$

### PHOSPHORUS AND OXYGEN

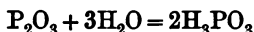
Phosphorus forms two oxides, the trioxide,  $P_2O_3$ , and the pentoxide,  $P_2O_5$ .

**PHOSPHORUS TRIOXIDE.**—Phosphorous oxide, or anhydride,  $P_2O_3$ , is produced when phosphorus is burnt with a limited supply of dry air. It is also formed when phosphorus is slowly oxidised in air. It is a white powder, which unites energetically with water to produce phosphorous acid,  $H_3PO_3$ .

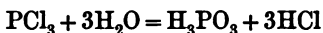
**PHOSPHORUS PENTOXIDE.**—Phosphoric oxide, or anhydride,  $P_2O_5$ , is produced when phosphorus undergoes complete combustion in an excess of dry air or oxygen. It may be conveniently prepared by burning fragments of phosphorus in a large glass globe, replacing the air at intervals. It is a snow-white powder, having a great affinity for water, even removing that fluid from sulphuric acid—a property which renders it of great

use for the drying of gases in the laboratory. Placed in water, union takes place, accompanied with a hissing noise resembling the quenching of a hot iron, the compound formed being ordinary tribasic phosphoric acid,  $\text{H}_3\text{PO}_4$ .

PHOSPHOROUS ACID,  $\text{H}_3\text{PO}_3$ , is formed when phosphorous oxide unites with water :—

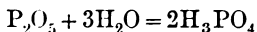


It may, however, be more conveniently prepared by the action of water on phosphorus triiodide or trichloride, thus :—



The hydrochloric acid produced may be driven off by boiling the liquid, which on cooling will deposit crystals of phosphorous acid. These crystals melt at  $76^\circ$ . Phosphorous acid is a powerful reducing agent, taking up oxygen from the substances exposed to its action, and becoming phosphoric acid. It is a strong acid, which is generally dibasic, and produces two classes of salts, in the one of which one of the constituent hydrogen atoms is replaced by a base; and in the other, two atoms of the hydrogen are so replaced. Calling the base M, and assuming it to be a monad, the general formulæ of the two classes of salts will be  $\text{H}_2\text{MPO}_3$ , and  $\text{HM}_2\text{PO}_3$ .

PHOSPHORIC ACID, tribasic phosphoric acid, trihydrogen phosphate, orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is the product formed by adding phosphorus pentoxide to water, and subsequently boiling the solution :—



Orthophosphoric acid may be more conveniently prepared by acting on phosphorus with nitric acid. The solution, concentrated at a gentle heat to a syrupy consistency, is then placed in a dissicator over oil of turpentine, when the pure acid is obtained in hard, transparent crystals.

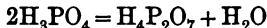




tained from a known weight of bone-ash. Thus 100 lbs. of bone-ash would contain 90 lbs. of the compound  $\text{Ca}_3\text{2PO}_4$ , the equivalent of which is 310, containing 62 parts of phosphorus; the 90 lbs. of  $\text{Ca}_3\text{2PO}_4$  contain therefore 18.0 lbs. of phosphorus. The equivalent of sodium phosphate,  $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ , is 358, containing 31 parts of phosphorus. The 18 lbs. of phosphorus contained in the 100 lbs. of bone-ash would thus yield 208 lbs. of  $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ .

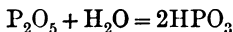
Besides the ordinary tribasic phosphoric acid, which is also for the sake of distinction called orthophosphoric acid, there are two other varieties—viz., pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , which is tetrabasic, and metaphosphoric acid,  $\text{HPO}_3$ , which is monobasic.

*Pyrophosphoric Acid*,  $\text{H}_4\text{P}_2\text{O}_7$ , may be obtained by heating orthophosphoric acid to a temperature of  $210^\circ$  to  $215^\circ$ , when the change takes place by loss of a molecule of water :—



The acid may be obtained in opaque, indistinct crystals, by the concentration of its aqueous solution. Common phosphate of soda yields sodium pyrophosphate by loss of water, thus  $2\text{Na}_2\text{HPO}_4 = \text{H}_2\text{O} + \text{Na}_4\text{P}_2\text{O}_7$ , when heated to redness. The four atoms of hydrogen in pyrophosphoric acid are each replaceable by equivalent quantities of a monad base forming four classes of salts, the neutral compound being that in which the whole of the hydrogen is so replaced; the other salts being more or less acid.

*Metaphosphoric Acid*,  $\text{HPO}_3$ , is the first product of the action of cold water on phosphoric oxide :—



It may also be produced by heating orthophosphoric acid to redness, water being given off—



Metaphosphoric acid is also produced by heating pyrophosphoric acid to redness—



The acid forms a glassy mass, which is the so-called “glacial phosphoric acid” of commerce. It is monobasic, and forms a class of salts called metaphosphates.

If microcosmic salt, the double phosphate of soda and ammonia,  $\text{Na}(\text{NH}_4)\text{HPO}_4$ , is heated to redness, it loses water and ammonia, and becomes sodium metaphosphate,  $\text{NaPO}_3$ .

The relation of the three modifications of phosphoric acid is simply a question of hydration. Starting with orthophosphoric acid, we find it convertible into pyrophosphoric acid by a loss of water, and into metaphosphoric acid by a further dehydration. On boiling, however, a solution of the latter acid it takes up water and passes to the full state of hydration, becoming converted into ordinary or orthophosphoric acid. Each of the three acids gives distinct and characteristic reactions, and may be recognised by distinctive tests, as shown in the following table :—

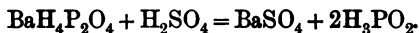
[TABLE

*Table giving the Distinctive Tests of the Three Varieties of Phosphoric Acid:—*

NAME	FORMULA	WITH $\text{AgNO}_3$	REACTION OF THE SOLUTION TO TEST PAPER AFTER ADDITION OF $\text{AgNO}_3$	ACTION ON SOLUTION OF ALBUMEN
Orthophosphoric Acid	$\text{H}_3\text{PO}_3$	Canary Yellow precipitate of $\text{Ag}_3\text{PO}_4$	Strongly acid	No action
Pyrophosphoric Acid	$\text{H}_4\text{P}_2\text{O}_7$	White precipitate of $\text{Ag}_4\text{P}_2\text{O}_7$	Neutral	No action
Metaphosphoric Acid	$\text{HPO}_3$	White gelatinous precipitate of $\text{AgPO}_3$	Neutral	Causes Coagulation

Orthophosphoric acid is also characterised by giving, on the addition of ammonia, ammonium chloride and magnesium sulphate, a white crystalline precipitate of the double phosphate of magnesia and ammonia,  $\text{NH}_4\text{MgPO}_4 + 6\text{H}_2\text{O}$ , when the mixture is briskly agitated.

*Hypophosphorous Acid*,  $\text{H}_3\text{PO}_2$ , is best prepared by decomposing the barium salt with an equivalent of sulphuric acid—



It is, when pure, a viscid uncrystallisable liquid, having a strongly acid reaction, and forming a class of salts called hypophosphites. The sodium compound may be prepared by boiling phosphorus with solution of caustic soda.

The subjoined table shows, in a concise form, the properties and methods of preparation of the oxides and oxacids of phosphorus :—

[TABLE

*Table showing the Methods of Preparation and Leading Characteristics of the Oxides and Oxacids of Phosphorus:—*

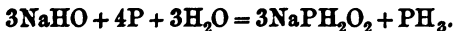
NAME	FORMULA	METHOD OF PREPARATION	LEADING CHARACTERISTICS
Phosphorus Trioxide or Phosphorous Anhydride	$P_2O_3$	By burning phosphorus with a limited supply of air or oxygen. $2P + 3O = P_2O_3$	White powder which unites energetically with water to form phosphorous acid.
Phosphorus Pentoxide or Phosphoric Anhydride	$P_2O_5$	By burning phosphorus in excess of air or oxygen. $2P + 5O = P_2O_5$	Snow white powder unites energetically with water to form phosphoric acid; it is very hygroscopic, and hence useful as a desiccating agent.
Phosphorous Acid or Hydrogen Phosphite	$H_3PO_3$	By the union of phosphorus trioxide with water— $P_2O_3 + 3H_2O = 2H_3PO_3$ By the action of water on phosphorous trichloride— $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$	When pure forms colourless crystals which melt at $60^\circ$ . Is a powerful reducing agent, and a strong acid. It is generally dibasic, and it forms phosphites with bases.

Table—Continued

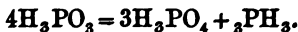
NAME	FORMULA	METHOD OF PREPARATION	LEADING CHARACTERISTICS
Ortho- Phosphoric Acid	$H_3PO_4$	$H_3PO_4$ is the ultimate product of the action of water on phosphorus pentoxide, the solution being boiled— $P_2O_5 + 3H_2O = 2H_3PO_4$ Also of the action of nitric acid on phosphorus.	$H_3PO_4$ in the pure state forms hard transparent crystals, very soluble in water, forming a strongly acid solution. The acid is tribasic, and forms three series of salts known generally as the orthophosphates.
Pyro- Hydrogen	$H_4P_2O_7$	$H_4P_2O_7$ is obtained when $H_3PO_4$ is heated to $210^\circ$ to $215^\circ$ — $2H_3PO_4 = H_4P_2O_7 + H_2O$	$H_4P_2O_7$ may be obtained in small opaque, indistinct crystals. It is tetrabasic, and forms four classes of salts.
Meta- Phosphate	$HPO_3$	$HPO_3$ is formed whenever $H_3PO_4$ or $H_4P_2O_7$ is heated to redness— $H_3PO_4 = HPO_3 + H_2O$ $H_4P_2O_7 = 2HPO_3 + H_2O$	$HPO_3$ generally occurs as a glassy transparent mass from which characteristic it derives its name of "glacial phosphoric acid." It is monobasic.
Hypophosphorous Acid	$H_3PO_2$	By decomposing the barium compound with an equivalent of sulphuric acid— $BaH_4P_2O_4 + H_2SO_4 = BaSO_4 + 2H_3PO_2$	A viscid, uncrystallisable liquid of extremely acid reaction. It possesses reducing properties, and forms salts with bases.

## PHOSPHORUS AND HYDROGEN

**HYDROGEN PHOSPHIDE**, phosphuretted hydrogen,  $\text{PH}_3$ , is usually prepared by the action of a solution of caustic potash, or caustic soda, on phosphorus, with the aid of heat.



The phosphuretted hydrogen is evolved as a gas. It may be obtained in a purer form by heating phosphorous acid.



The phosphuretted hydrogen prepared by the action of a caustic alkali on phosphorus, inflames spontaneously on contact with air, a property due to the presence of traces of the liquid compound  $\text{P}_2\text{H}_4$ , which can be separated by passing the gas through a tube immersed in a freezing mixture. In preparing this spontaneously inflammable form of phosphuretted hydrogen, small quantities of the materials should be placed in a small retort, the end of the neck dipping under water. Heat should be applied cautiously at first. When the evolution of the gas has commenced, a most singular phenomena will be observed. Each bubble of the gas, as it rises to the surface of the water, catches fire with a bright flash, and produces a ring of phosphorus pentoxide which enlarges as it ascends, presenting a most beautiful appearance. Phosphuretted hydrogen is characterised by possessing an unpleasant odour, resembling that of stinking fish. Besides the gaseous compound  $\text{PH}_3$ , there is also the liquid phosphide  $\text{P}_2\text{H}_4$ , and a solid phosphide,  $\text{P}_4\text{H}_2$ .

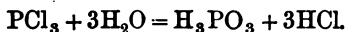
## PHOSPHORUS AND CHLORINE

Two compounds of phosphorus and chlorine are known, viz., phosphorus trichloride,  $\text{PCl}_3$ , and phos-



phorous pentachloride,  $\text{PCl}_5$ . An oxychloride,  $\text{PCl}_3\text{O}$ , is also known.

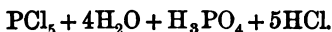
PHOSPHORUS TRICHLORIDE, phosphorous chloride,  $\text{PCl}_3$ , is prepared by passing slowly a current of chlorine gas over melted phosphorus contained in a retort. It is a colourless fuming liquid of offensive odour. It has a specific gravity of 1.5, and boils at  $73.8^\circ$ . Placed in contact with water it slowly decomposes, forming phosphorous and hydrochloric acids.



PHOSPHORUS PENTACHLORIDE, phosphoric chloride,  $\text{PCl}_5$ , is formed when phosphorus is heated in an excess of chlorine, and also by the action of chlorine on phosphorus trichloride. It is a white or yellowish coloured crystalline solid. It may be sublimed at  $100^\circ$ , and in contact with a limited quantity of water, hydrochloric acid and phosphorus oxychloride are formed thus :—



With an excess of water, phosphoric and hydrochloric acids are the sole products formed thus :—



Phosphorus oxychloride may be procured in a state of purity by heating the pentachloride with the pentoxide.

Phosphorus unites with bromine to form compounds analagous with those of chlorine, with iodine to form the compounds  $\text{PI}$  and  $\text{PI}_3$ , and with sulphur it gives the compounds  $\text{P}_2\text{S}_3$ , and  $\text{P}_2\text{S}_5$ .

The volume occupied by the atom of phosphorus weighing thirty-one is only half as large as that occupied by the atoms of the majority of the other elements, the vapour density is consequently *twice* the atomic weight—viz, sixty-two.

## CHAPTER VI.

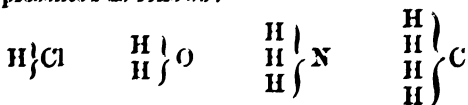
## THE HIGHER PRINCIPLES OF CHEMICAL PHILOSOPHY

THE elementary principles of chemical philosophy have already been discussed, and it therefore only remains to briefly mention some of the leading principles of chemical science, which, being of a more advanced nature, may be more advantageously discussed here. These include explanations of the doctrines of atomicity, compound radicals, varieties of chemical formulæ, the classification of salts, types, the different modes of chemical action; the relation of atomic weight to specific heat; heat of combination, the method of calculating the empirical formula of a substance from its percentage composition, and the principles of crystallography.

## VALENCY OR ATOMICITY OF ELEMENTS

The term *Valency*, sometimes termed *Quantivalence*, and sometimes *Atomicity*, is used to express the comparative saturating power of the different elements, taking hydrogen as the unit. Thus the atom replacing, or atom saturating power of the elements, varies greatly. We find for instance the compound HCl containing single equivalents of chlorine and hydrogen, the compound H<sub>2</sub>O containing two equivalents of hydrogen to one of oxygen, while in ammonia, NH<sub>3</sub>, we have three equivalents of hydrogen to one of nitrogen, and in marsh gas, CH<sub>4</sub>, four of hydrogen to one of carbon.

We thus form the conclusion that chlorine requires for saturation one equivalent of hydrogen, oxygen two, nitrogen three, and carbon four. The compounds may be represented as follows:—



Turning to other elements and compounds, similar relations may be observed, and we may distinctly mark out broad groups containing different quantities of hydrogen, thus:—

	Hydrogen	Hydrochloric Acid	Hydrobromic Acid	Hydriodic Acid	Hydrofluoric Acid
1.	HH	HCl	HBr	HI	HF
	Water	Sulphuretted Hydrogen	Seliniuretted Hydrogen	Telluretted Hydrogen	
2.	$\begin{matrix} \text{H} \\ \text{H} \end{matrix} \bigg\} \text{O}$	$\begin{matrix} \text{H} \\ \text{H} \end{matrix} \bigg\} \text{S}$	$\begin{matrix} \text{H} \\ \text{H} \end{matrix} \bigg\} \text{Se}$	$\begin{matrix} \text{H} \\ \text{H} \end{matrix} \bigg\} \text{Te}$	
	Ammonia	Phosphuretted Hydrogen	Arseniuretted Hydrogen		
3.	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix} \bigg\} \text{N}$	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix} \bigg\} \text{P}$	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix} \bigg\} \text{As}$		
	Marsh Gas	Siliciuretted Hydrogen			
4.	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{matrix} \bigg\} \text{C}$	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{matrix} \bigg\} \text{Si}$			

Elements are thus classified according to their various atomicities into monads, dyads, triads, tetrads, pentads, and hexads, and are imagined for the sake of explanation to have a corresponding number of points of attachment or bonds of union with which to unite with other elements. It must be understood that the affinity of these bonds may be saturated by an equal number of bonds of some other element. The *absolute atomicity* of an element is generally taken to be the largest number of bonds of union which it satisfies in any of its compounds. It, however, frequently happens, that a less number of bonds are engaged; in every case the number of engaged bonds is spoken of as the *active atomicity*, while to the number not so taken up,

the term *latent atomicity* is applied. Sulphur, for instance, is a hexad in sulphur trioxide,  $\text{SO}_3$ , where one atom of sulphur is united to three atoms of dyad oxygen; in sulphur dioxide,  $\text{SO}_2$ , it is a tetrad, while in sulphuretted hydrogen,  $\text{H}_2\text{S}$ , it is a dyad. Again, the element nitrogen is a triad in ammonia,  $\text{NH}_3$ , where it is united to three atoms of the monad hydrogen, a pentad in ammonium chloride,  $\text{NH}_4\text{Cl}$ , and only a monad in nitrous oxide,  $\text{N}_2\text{O}$ . In these two cases the highest atomicities are six in the case of sulphur, and five in the case of nitrogen; the former is, therefore, regarded as a hexad, and the latter as a pentad. The disappearance of the active atomicity by twos, which is found to be always the case, has led Dr Frankland to suggest that the bonds of union so disappearing are engaged in satisfying each other.

It is worthy of note that although the valency of an element varies in its different compounds, such variation always takes place in a particular way, by which the active atomicity of an element whose absolute atomicity is even, always remains even, while in those having an uneven absolute atomicity, the active atomicity is always uneven. Thus nitrogen is a monad, triad, or pentad, but never dyad or hexad. Sulphur, on the other hand, is dyad, tetrad, or hexad, but never triad or pentad. The elements are thus divided into *Perissads* (atomicity odd), and *Artiads* (atomicity even).

*The following Table gives a List of the Leading Elements classed according to their Atomicity :—*

PERISSADS			ARTIADS		
MONADS	TRIADS	PENTADS	DYADS	TETRAADS	HEXADS
HYDROGEN * CHLORINE * BROMINE * IODINE * FLUORINE * Potassium Sodium Lithium Silver Thallium	Boron Gold	Nitrogen Phosphorus Arsenic Antimony Bismuth	OXYGEN * Barium Strontium Calcium Magnesium Zinc Cadmium Copper Mercury	CARBON SILICON Tin Titanium Aluminium Platinum Palladium Lead	SULPHUR * SELENIUM * Chromium Manganese Iron Cobalt Nickel Uranium

The atomicity of an element is often expressed by appending Roman numerals to its symbol, thus :—

i	ii	iii	iv	v	vi
H	O	Au	C	N	S

In the foregoing table the elements marked with a star are *chlorous*, and the remainder *basyulous*. Chlorous or electro-negative elements are evolved at the negative pole, and basyulous or electro-positive elements are liberated at the positive pole, when their compounds are subjected to the action of an electric current. There is, however, no sharp distinction between the two classes, an element being chlorous in one compound and basyulous in another. One important fact in connection with the action of an electric current is that for every *equivalent* of zinc consumed in a galvanic cell, an *equivalent* of an element is liberated from its compounds. Thus in the decomposition of water, the liberation of 16 parts of oxygen is accompanied by the solution of 65·2 parts of zinc. This is also true in cases where a metal is precipitated by the immersion of another metal in its solution, such, for instance, as the precipitation of copper by iron, for one equivalent of copper precipitated, one equivalent of iron must be dissolved.

## COMPOUND RADICALS

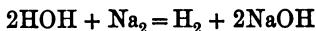
The term, compound radical, is used to define certain definite groups of elements which are apparently capable of being transferred from one compound to another, and are often observed in similar classes of substances. Thus, sulphuric acid may be assumed to contain the compound radical  $\text{SO}_2$ , united to the compound radical  $\text{OH}$ , thus  $\text{SO}_2(\text{OH})_2$ . The group  $\text{SO}_2$  may be traced all through the compounds of sulphuric acid, thus :—

$\text{SO}_2(\text{OK})_2$	$\text{SO}_2(\text{ONa})_2$	$\text{SO}_2\text{CuO}_2$
(Potassium sulphate)	(Sodium sulphate)	(Copper sulphate)

In like manner, nitric acid and the nitrates may be assumed to contain the group  $\text{NO}_2$ . The radical hydroxyl  $\text{OH}$  is supposed to play a part in all oxacids and hydroxides, thus :—



Acting on the hydride by sodium the hydroxyl-radical is transferred to sodium forming sodium hydroxide (caustic soda)—



Like the elements, these groups have different atomicities dependent on the number of unsaturated bonds

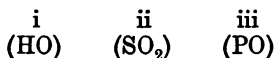
which they possess ; thus hydroxyl  $\text{H} \text{---} \text{O} \text{---}$

is monatomic, the radical  $\text{O} = \text{S} = \text{O}$  is a

dyad, while a triad radical  $\text{---} \text{P} = \text{O}$  is assumed

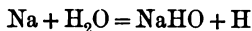
to exist in the phosphorus oxacids. Many other groups or radicals may be thus traced in different compounds. It must, however, be remembered that a large number of these radicals have never been isolated, and that therefore their existence is to a great extent hypothetical. The compound radical theory will, however, often be found a useful aid to the study of molecular constitution, and should be regarded mainly in that light.

The atomicity of the radical groups mentioned, like that of the elements, is often indicated by Roman numerals, thus :—



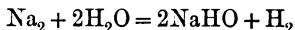
## VARIETIES OF CHEMICAL FORMULÆ

For the sake of simplicity, *atomic* and *empirical* formulæ have been, as a rule, used throughout the present work ; it is, however, necessary for the student to understand that such formulæ are not generally regarded as truly representing what takes place when chemical action occurs. For this purpose it is necessary to employ *molecular* and *rational*, sometimes called *structural* formulæ, while on some occasions *graphic formulæ* are preferable. In order to understand the distinction which exists between the different varieties of chemical formulæ, it will be best to give a few examples. Firstly, with regard to the distinction between the *atomic* and the *molecular*. It has been pointed out as extremely probable that a single atom of any elementary gas, or even of the elements generally, does not exist in the free state, but that the individual atoms unite with each other to form molecules, thus the atom of chlorine is represented by Cl, that of hydrogen by H, that of oxygen by O, and that of sodium by Na. *Free* chlorine, *free* hydrogen, *free* oxygen, and *free* sodium, however, are more correctly represented as *molecules*—thus, Cl<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, Na<sub>2</sub>. It is obvious, therefore, that such an equation as the following—

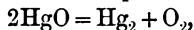


representing the action of sodium on water, although expressing what takes place in the simplest possible terms, is not in reality a correct equation.

The equation—

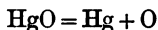


is the correct method of representation, a *molecule* in place of an *atom* of sodium being employed, and a molecule of free hydrogen being liberated. Again, in the production of oxygen by the action of heat on mercuric oxide, the correct expression is



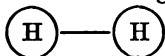


indicating the liberation of a *molecule* of mercury and of oxygen in place of writing



in which single atoms only are set free. The first is called a *molecular formula*, and the second an *atomic formula*. It will be seen that the two forms of expression always bear a simple relation to each other.

The theory of elements in the free state being molecules in place of atoms explains the great chemical energy manifested by elements in the nascent condition. Thus we have already noticed that whereas *free* hydrogen has very slight reducing properties, *nascent* hydrogen is capable of effecting many reductions in which great chemical energy is manifested. This is explained by the assumption that in *free* hydrogen (the molecule) the two single bonds of the two hydrogen atoms are engaged in satisfying each other, thus,



and these atoms must be separated before the hydrogen atoms can enter into fresh combinations. Where, however, hydrogen is liberated from any of its compounds, that is, when it is *in the nascent state*, the hydrogen atoms at the moment of their liberation are free to react on any substance which is present, and can thus effect changes of which the molecule is incapable. The same reasoning applies to the nascent condition of elements generally.

A further important distinction in the expression of chemical reactions by equations is dependent on the use of *empirical formulæ*, or of *rational formulæ*, sometimes called *symbolic*, *constitutional*, or *structural*. An empirical formula is generally the simplest possible expression of the composition of any compound, showing simply the number of constituent atoms without reference to their arrangement in the molecule. *Constitutional formulæ* aim at showing not only the composition of a compound, but as nearly as possible the

actual arrangement of the constituent atoms. Very little is, however, at present really known about molecular arrangement, beyond the fact that many compounds appear to possess a part of their constituent elements so grouped together as to permit of removal and substitution so as to form new compounds. In organic chemistry, more especially, these groups of elements, or *compound radicals*, as they are more generally called, play a most important part, and a knowledge of their character and functions has much simplified the study of organic compounds. In order to show the distinction between empirical and constitutional formulae, sulphuric acid may be taken as a familiar example. Sulphuric acid is generally written  $\text{H}_2\text{SO}_4$ . This formula gives the simplest possible expression of its composition, and shows it to be a compound of two atoms of hydrogen, one of sulphur, and four of oxygen, but there is no indication of the way in which the component elements are arranged in the molecule, and the formula is therefore termed *empirical*. The *rational* or *constitutional* formula for the same substance is  $\text{SO}_2(\text{HO})_2$ , which is a written representation of the way in which the atoms are supposed to be grouped in the compound—viz., that the four bonds of the hexad sulphur atom are satisfied by two atoms of dyad oxygen, while the two remaining bonds of the atom of sulphur are united to two hydroxyl radicals. The *graphic formula* of sulphuric acid will show this arrangement—



Again, the empirical formula for calcium hydrate is  $\text{CaH}_2\text{O}_2$ , which simply indicates the number of

constituent atoms present. The rational formula is written  $\text{Ca}(\text{HO})_2$ , showing that the dyad calcium is united to two hydroxyl radicals, and the graphic formula is—



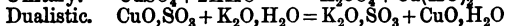
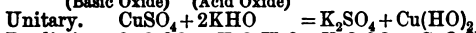
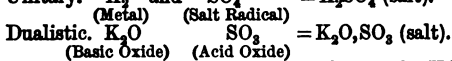
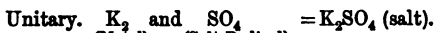
The system of rational formulæ, which is thus the written representation of graphic formulæ, is frequently termed *symbolic notation*. A further variety of formula, the glyptic, is used for lecture demonstrations, and consists of a series of coloured balls indicating the atoms of the different elements, provided with holes corresponding to the number of the bonds of union. By means of pegs the atoms may be attached to each other, and the various compounds suitably represented.

### CONSTITUTION OF SALTS

A salt has been already defined as a compound formed by the combination of an acid with a base. Salts may be generally divided into haloid salts, which is in the strictest sense confined to the compounds formed by the simple union of a halogen with a metal, such, for instance, as  $\text{NaCl}$ ,  $\text{KI}$ , etc.; and oxysalts formed by the union of an oxygen acid, or oxygenated salt radical, with a metal, such, for instance, as  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ , etc.

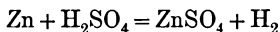
Two modes of representing the constitution of salts are in vogue—viz., the unitary system and the dualistic. By the first system, which is that now generally adopted, all salts are regarded as compounds of a metal with a salt radical—thus sulphuric acid is  $\text{H}_2\text{SO}_4$ , nitric acid  $\text{HNO}_3$ , phosphoric acid  $\text{H}_3\text{PO}_3$ , potassium sulphate,  $\text{K}_2\text{SO}_4$ , potassium nitrate  $\text{KNO}_3$ , and potassium hydrate  $\text{KHO}$ . This method of representation is objected to

by some chemists on the ground that it supposes the existence of salt radicals such as  $\text{SO}_4$ ,  $\text{NO}_3$ , and  $\text{PO}_3$ , which have not been isolated, and the existence of which is therefore purely hypothetical, while at the same time it ignores the radicals  $\text{SO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ , the existence of which is known. In the dualistic mode of expression these radicals are not ignored, and no hypothetical compounds are assumed to exist; thus, sulphuric acid is written  $\text{H}_2\text{O}, \text{SO}_3$ , nitric acid  $\text{H}_2\text{O}, \text{N}_2\text{O}_5$ , phosphoric acid  $\text{H}_2\text{O}, \text{P}_2\text{O}_5$ , potassium sulphate  $\text{K}_2\text{O}, \text{SO}_3$ , potassium nitrate  $\text{K}_2\text{O}, \text{N}_2\text{O}_5$ , and potassium hydrate  $\text{K}_2\text{O}, \text{H}_2\text{O}$ . The following equations will illustrate the methods of representing chemical action by the two modes of expression:—



Again, the formula for potash alum is by the unitary method  $\text{Al}_2\text{K}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ , while by the dualistic mode of expression it is  $\text{Al}_2\text{O}_3, 3\text{SO}_3, \text{K}_2\text{OSO}_3 + 24\text{H}_2\text{O}$ .

A SALT is regarded in the unitary system as a compound derived from an acid by the displacement of hydrogen by a metal—example, formation of zinc sulphate—



A normal salt is a compound derived from an acid by the substitution of a metal for the whole of its displaceable hydrogen. Example, potassium sulphate,  $\text{K}_2\text{SO}_4$ . An acid salt is a compound derived from an acid by the substitution of a metal for a part of its displaceable hydrogen. Example, hydrogen potassium sulphate,  $\text{KHSO}_4$ .

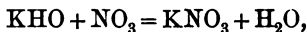
A double salt is a compound derived from an acid by

*the substitution of different metals for its displaceable hydrogen.* Example, potash alum  $\text{Al}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$ . A *basic salt* is a combination of a salt with a basic oxide.

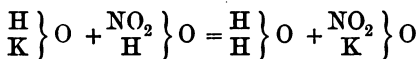
By the dualistic theory the definition of the different kinds of salts is not so simple, and the classification is based on the ratio of the oxygen in the base to the oxygen in the acid, the ratio for the neutral salt being different in acids of different basicity.

### TYPES

Among the many ways of writing the formulæ of chemical compounds, it is sometimes convenient to represent each substance as built on a certain *type*. Such a mode of representation will frequently be found to facilitate the comprehension of those chemical changes in which a substance is changed by the elimination of an element or group of elements, and the substitution of a fresh element or group—thus, in place of writing



showing the formation of potassium nitrate and water from potassium hydrate and nitric acid, we may write the equation—



In this equation the compounds are represented on the type of water  $\left. \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\} \text{O}$ .

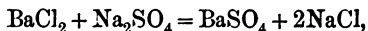
The majority of chemical substances may be referred

to one of the following types, viz., Hydrochloric Acid, Water, Ammonia, and Marsh Gas, thus :—

Hydrochloric Acid	$\begin{matrix} \text{H} \\ \text{Cl} \end{matrix}$	Potassium Chloride	$\begin{matrix} \text{K} \\ \text{Cl} \end{matrix}$	Ethyl Hydride	$\begin{matrix} \text{C}_2\text{H}_5 \\ \text{H} \end{matrix}$	
Ammonia	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	N. Phosphuretted Hydrogen	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	P. Formamide	$\begin{matrix} \text{CHO} \\ \text{H} \\ \text{H} \end{matrix}$	N
Marsh Gas	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	C. Methyl Chloride	$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{Cl} \end{matrix}$	C. Amylene	$\begin{matrix} \text{CH}(\text{CH}_3)_2 \\ \text{CH}_2 \\ \text{H} \\ \text{CH} \end{matrix}$	C

## MODES OF CHEMICAL ACTION

The preparation of the various elementary and compound bodies involves the use of distinct chemical processes, dependent on distinct modes of action. The two divisions of chemical action, synthesis, and analysis, have already been alluded to. A common mode of action is double decomposition, thus—



in which the two bodies, acting on each other, are both decomposed, a mutual transfer of acids and bases occur, and two entirely distinct compounds are formed. When substances of a different nature are brought together, the action which occurs is dependent on many conditions, temperature, pressure, physical condition, whether liquid, solid, or gaseous, and on the so-called chemical affinity. Chemical affinity is generally used to express the *chemical* attraction which one substance possesses for another. Thus, when sodium chloride is heated with sulphuric acid, the conversion of the sodium chloride into sodium sulphate is said to occur because the sodium and the sulphuric acid have a greater chemical affinity for each other than the sodium and the chlorine.

Dr Frankland has classified the various methods by which chemical action takes place, as follows :—

1. A direct combination of elements or compounds with each other.

Examples :— $\text{Na} + \text{Cl} = \text{NaCl}$ .       $\text{HCl} + \text{NH}_3 = \text{NH}_4\text{Cl}$ .

2. A displacement of one element or compound radical in a body by another element or compound radical.

Example :— $\text{H}_2\text{SO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{H}_2$

3. A mutual exchange of elements or compound radicals in two or more bodies.

Example :— $\text{NaCl} + \text{AgNO}_3 = \text{AgCl} + \text{NaNO}_3$

4. A re-arrangement of the elements or compound radicals already contained in a body.

Example :— $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$

5. The resolution of a compound into its elements or into two or more less complex substances.

Examples :— $\text{HgO} = \text{Hg} + \text{O}$ .

$\text{Pb}(\text{NO}_3)_2 = \text{PbO} + \text{N}_2\text{O}_4 + \text{O}$ .

### SPECIFIC AND ATOMIC HEAT

The term *specific heat* is used to define the absolute amount of heat which is required to raise a given weight of any substance through a given range of temperature, water being taken as the unit of comparison. This absolute quantity differs very widely in the different elements, as well as in their compounds, and substances are therefore said to possess *different capacities for heat*. For instance, calling the amount of heat necessary to raise a kilogram of water one degree, 1·0, the quantity of heat necessary to raise the same weight of zinc, of platinum, or of silver, through the same range of temperature is expressed by the numbers 0·095, 0·031, and 0·059, respectively. The specific heat of silver is therefore said to be ·059, that of plati-

num  $\cdot 031$ , and that of zinc  $\cdot 095$ . A singular relation has been observed between the specific heats of the elements and their atomic weights, viz., that the product of the multiplication of the one by the other is in most cases a constant quantity, and thus the *atomic heat*, or specific heat of the atoms of the elements in a solid state, is in most cases also a constant quantity, and specific heat is therefore a mode of checking atomic weight. The following table shows this relation in a few selected elements by way of illustration :—

Elements	Specific Heat	Atomic Weight	Product of Multi- plying Specific Heat by Atomic Weight
Lithium	0.9408	7	6.59
Sulphur	0.2026	32	6.48
IRON	0.1138	56	6.37
Zinc	0.0956	65.2	6.24
Silver	0.0590	108	6.37
Iodine	0.0541	127	6.87
Gold	0.0324	197	6.38
Bismuth	0.0308	210	6.48

All the elements agree to this relation, with the exception of phosphorus, fluorine, oxygen, silicon, boron, hydrogen, and carbon; of these the greatest variation is exhibited in the cases of carbon, hydrogen, boron, and silicon. Taking all the elements which exhibit a fairly constant relation between specific heat and atomic weight, the mean *atomic heat* comes to 6.4. The best mode of determining specific heat is by mixing equal weights of water at  $100^{\circ}$ , and the substance to be examined, and observing what loss of temperature the water suffers in raising the temperature of the substance through a certain number of degrees. Another method is to observe how much ice is melted by a given weight of the substance heated to a given temperature. Many corrections have to be made, and it is difficult to get



correct results. The specific heat of bodies not known in the solid state, such, for instance, as nitrogen or chlorine, has to be determined from an examination of their compounds with elements, the specific heat of which is previously known.

	Specific Heat	Molecular Weight	Product of specific heat and Molecular Weight
Silver Chloride $\text{AgCl}$	0.089	143.5	12.77
Sodium Chloride $\text{NaCl}$	0.219	58.5	12.81

Taking the atomic heats of silver and sodium as 6.4, and deducting that number from 12.77 and 12.81, we get 6.37 and 6.41, two fairly agreeing numbers. The atomic heat of chlorine in the solid state, therefore, agrees with the number 6.4.

Again, in carbon, which does not possess the same atomic heat, the specific heat of one of its compounds, viz., the hexachloride  $\text{C}_2\text{Cl}_6$  is .177, which, multiplied by the molecular weight (237) gives 42.0. Now, as the atomic heat of solid chlorine has been shown to be 6.4, and the compound contains six equivalents of chlorine  $6.4 + 6 = 38.4$ , which, deducted from 42.0, gives 3.6 as a residue for the atomic heat of the two carbon atoms, and the atomic heat of the single atom is therefore  $3.6 \div 2 = 1.8$ . Although the fixed relation of atomic weight to specific heat does not hold good for all the elements, this relation is often expressed as a law, thus: "*the specific heat of an element in the solid state is inversely proportional to its atomic weight.*" This is called the law of Dulong and Petit.

### HEAT OF COMBINATION

One of the most commonly occurring phenomena in the chemical union of substances is the evolution of heat, of which ordinary combustion, the union of combustible bodies with oxygen, is a familiar example. *The amount of heat evolved in the union of many*

substances has been determined ; and the respective quantities are called the *heats of combination*. In the case, however, of the union of combustible bodies with oxygen, the heat evolved is generally spoken of as the *heat of combustion*. The determination of the heat of combination is attended with great difficulties in order to obtain accurate results, in consequence of the fact that changes in chemical condition are usually attended with changes in physical condition, for which due allowance has to be made. The heat of combustion is generally measured by burning a known weight or volume of the combustible substance in an excess of pure oxygen in a copper vessel immersed in water, and noticing the number of degrees which the water rises in temperature ; many precautions have to be observed and corrections made in order to ensure accurate results. In cases where the union of substances only evolves a moderate amount of heat, a different process for the determination of the heat evolved is employed. One process used in the case of substances soluble in water, such as acids and alkalies, is by mixing dilute solutions of the two substances, and observing the rise of temperature, while in another method the substances are introduced separately into small tubes inserted into the bulb of a thermometer having a large bulb connected to a comparatively small tube. When the substances to be tested are mixed, the expansion of the mercury gives an indication of the amount of heat evolved. The above descriptions are necessarily brief, and for the details of the precautions to be observed in order to secure accurate results, the student is referred to the larger text books. It has been repeatedly proved by experiment that the heat evolved from the combustion of a hydrocarbon is not so great as that evolved from the combustion of its constituent elements separately. This arises from the fact that in combustion a certain amount of the heat evolved is absorbed in causing the separation of the constituent elements of the hydro-

carbon, and the amount of heat thus disappearing is identical with the amount evolved by their union. For instance, a certain amount of heat is produced when carbon unites with hydrogen to form marsh gas, and the heat evolved from the combustion of a given quantity of this compound is found to be less than is obtained from the combustion of its hydrogen and (gaseous) carbon separately. In the case of the combustion of solid and liquid hydrocarbons, a further quantity of heat is absorbed in the conversion of their constituted elements to the gaseous state.

#### CALCULATION OF THE EMPIRICAL FORMULA OF A SUBSTANCE FROM ITS PERCENTAGE COMPOSITION

This problem is often presented for solution in chemical research, and the method of calculation will be best shown by some illustrations. Let us assume that a compound of silver and chlorine has been analysed and found to contain

Silver . .	75·26
Chlorine . .	24·74
	<hr/>
	100·00

If these percentage numbers are divided by the respective atomic weights, we shall get *the relation between the combining weights*, thus :—

$$\frac{75\cdot26}{108} = \cdot696, \text{ and } \frac{24\cdot74}{35\cdot5} = \cdot696$$

The relation of combining weights is, therefore, ·696 to ·696 or as units, and the compound contains *single equivalents* of silver and chlorine, that is, 108 of silver to 35·5 of chlorine, and its formula is, therefore, AgCl. Again, a substance on analysis has yielded per cent.,

Potassium . .	69·70	} 100·00
Oxygen . .	28·52	
Hydrogen . .	1·78	

Dividing each number by the equivalent weight of the respective element we have—

$$\frac{69.70}{39.1} = 1.78 \quad \frac{28.52}{16} = 1.78 \quad \frac{1.78}{1} = 1.78$$

The relation between the combining weight is, therefore, 1.78 to 1.78 to 1.78, that is, as units, and the empirical formula is, therefore, KHO.

Taking a further example, let us assume that a compound has given an analysis in 100 parts.

Manganese . .	69.62
Oxygen . .	30.38

Proceeding as before,

$$\frac{69.62}{55} = 1.265 \quad \frac{30.38}{16} = 1.899$$

Now 1.265 to 1.899 is as 1 to 1.5, and multiplying by two to convert into whole numbers, the ratio is as two to three, and the simplest formula is therefore  $\text{Mn}_2\text{O}_3$ .

The relation between the percentage composition of a substance and its formula will be again referred to in organic chemistry.

#### CALCULATION OF THE PERCENTAGE COMPOSITION OF A SUBSTANCE FROM ITS FORMULA

This is accomplished as follows:—

Supposing it is wished to ascertain the percentage composition of iron pyrites,  $\text{FeS}_2$ .

The molecular weight is first obtained,  $\text{Fe} = 56$  and  $\text{S}_2 = 32 \times 2 = 64$ . The molecular weight is therefore  $56 + 64 = 120$ . Of these 120 parts 56 are iron; to find, therefore, how much iron exists in 100 parts—

$$120 : 100 :: 56 : x \\ x = 46.66$$

Then in the same way to calculate the sulphur—

$$120 : 100 :: 64 : x$$

$$x = 53.33$$

The percentage composition of  $\text{FeS}_2$  is therefore—

Fe	46.66
S	53.33
<hr/>	
	99.99

It will be seen that the following simple rule can be deduced from the preceding calculations:—*To find the percentage composition of a compound from its formula, multiply the amount of each element present by 100, and divide by the molecular weight of the compound.*

Thus, taking crystallised magnesium sulphate as an example, the formula of which is  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , the molecular weight will be  $24(\text{Mg}) + 32(\text{S}) + 64(\text{O}_4) + 126(7\text{H}_2\text{O}) = 246$ . Proceeding by the rule, and taking the magnesium first—

$$\frac{24 \times 100}{246} = 9.756$$

Then for sulphur—

$$\frac{32 \times 100}{246} = 13.008$$

Then for oxygen—

$$\frac{64 \times 100}{246} = 26.01$$

Finally for water of crystallisation—

$$\frac{126 \times 100}{246} = 51.219$$

The percentage composition is therefore—

Magnesium . . . .	9.756
Sulphur . . . .	13.008
Oxygen . . . .	26.016
Water of crystallisation .	51.219
	<hr/>
	99.999

In the same way the percentage composition of mercurous chloride (calomel),  $\text{HgCl}_2$ , may be calculated, its molecular weight being 235.5. The composition per cent is—

Mercury . . . .	84.925
Chlorine . . . .	15.075
	<hr/>
	100.000

Mercuric chloride, or corrosive sublimate,  $\text{HgCl}_2$ , molecular weight 270, will be found to contain per cent—

Mercury . . . .	74.074
Chlorine . . . .	25.926
	<hr/>
	100.000

While oxalic acid,  $\text{C}_2\text{H}_2\text{O}_4$ , molecular weight 90, contains—

Carbon . . . .	26.666
Hydrogen . . . .	2.222
Oxygen . . . .	71.111
	<hr/>
	99.999

## CRYSTALLOGRAPHY

The several elements and compounds known in inorganic, as well as in organic, chemistry, are divided into those which cannot be obtained in any geometrical form, and which are termed *amorphous*, and those

which crystallise or assume a definite geometrical form, and which are called *crystalline*. Substances in the crystalline form exhibit several peculiar characteristics; beyond possessing a definite shape, they have a tendency to split with greater facility in certain directions than in others, a property known as cleavage; they also in many cases allow the passage of heat and light rays more readily in one direction than another. The last named characteristic gives rise to the phenomena of double refraction. Each crystallisable substance, assumes as a rule a distinct and characteristic form of crystallisation; but some bodies, on the other hand, are known in two distinct crystalline forms. This is termed *dimorphism*. Among the elements, sulphur and carbon may be taken as examples of dimorphism, whilst among compounds may be mentioned calcium carbonate, arsenious oxide, and magnesium sulphate. Among crystallisable substances crystals are generally procured by taking advantage of the fact that a hot solution is capable of retaining more of the substance than a cold solution. To procure the crystals of any crystallisable substance, a *supersaturated* solution is made by the aid of heat, which deposits the excess of the dissolved material in the crystalline form on cooling the solution, and the slower the rate at which the cooling takes place, the larger and more perfect in form are the crystals produced. In some cases the crystals of a substance which separate from the aqueous solution, do not retain any water, and are then termed *anhydrous*, while in other cases a certain amount of water is retained by the crystals, and is necessary for the maintenance of their crystalline form. The amount of water so retained is always in definite chemical proportion, and is known as *water of crystallisation*; this is, as a rule, easily expelled by exposure to a moderate heat. Compounds of different chemical composition sometimes assume the same crystalline form, and such compounds are termed *isomorphous*.

Isomorphous bodies not only possess the same crystalline form, but also exhibit certain similarities in structure and composition. As an illustration, the alum series, the spinel series, and the vitriol series, may be quoted. As examples of the alums, the following may be quoted :—

Ammonia alum	.	$\text{Al}_2(\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$
Soda alum	.	$\text{Al}_2\text{Na}_2\text{SO}_4 + 24\text{H}_2\text{O}$
Potash alum.	.	$\text{Al}_2\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$
Chrome alum	.	$\text{Cr}_2\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$
Iron alum	.	$\text{Fe}_2\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$

It will be noticed that all these compounds, besides crystallising in the same form (the regular system), contain the same number of equivalents of water of crystallisation, and of the sulphuric acid radical, and also the same number of equivalents of base. The spinel series also crystallise on the regular system. The following examples will suffice :—

Spinel	.	$\text{MgOAl}_2\text{O}_3$
Magnetic iron ore	.	$\text{FeOFe}_2\text{O}_3$
Chlorspinel	.	$\text{MgOFe}_2\text{O}_3$
Chrome iron ore	.	$\text{FeOCr}_2\text{O}_3$

Of the vitriol series the following examples may be given, crystallising in the monoclinic system :—

Zinc sulphate	.	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$
Magnesium sulphate	.	$\text{MgSO}_4 + 7\text{H}_2\text{O}$
Iron sulphate	.	$\text{FeSO}_4 + 7\text{H}_2\text{O}$
Nickel sulphate	.	$\text{NiSO}_4 + 7\text{H}_2\text{O}$

The phenomenon of isomorphism often affords considerable assistance in fixing the atomicity of an element, for if in two elements, both affording isomorphous compounds, the atomicity of the one is known, that of the other can be inferred.



The following table exhibits the characteristic features of the six crystallographic systems, into which the various crystalline forms have been classified, together with examples of each system. In the different forms certain *lines* called *axes* are assumed to exist within the crystal, about which the form may be symmetrically arranged :—

[TABLE

*examples of each :—*

	CHARACTERISTIC FEATURES	SIMPLEST FORMS	EXAMPLES
1	The Regular System Three axes, all equal and at right angles	The Cube. The regular octahedron. The rhombic dodecahedron. The regular tetrahedron	The diamond. Alum. Common salt. Fluor spar. Iron pyrites. Garnet.
2	The Quadratic System Three axes, one shorter or longer than the other two, and all at right angles	The square prism The square octahedron	Potassium ferrioxanide. Zircon. Tin dioxide
3	The Hexagonal System Four axes, three equal, and in one plane at an angle of $60^\circ$ , and one longer or shorter at right angles to the other three	Regular six sided prism The Rhombohedron	Quartz. Calc Spar. Graphite. Ice. Corundum
4	The Rhombic System Three axes, all unequal, and all at right angles	The right octahedron with rhombic base The right rhombic prism The oblique rhombic octahedron	Native Sulphur. Arragonite. Topaz. Barium Sulphate. Potassium Nitrate Sodium phosphate, and carbonate. Ferrous sulphate. Cane Sugar. Borax
5	The Monoclinic System Three axes, all unequal, two cutting each other obliquely, and one at right angles to the plane of the other two		
6	The Triclinic System Three axes, all unequal, and all oblique	The doubly oblique octahedron, and doubly oblique prism	Potassium Dichromate. Boracic acid. Copper sulphate

## CHAPTER VII.

THE CHEMISTRY OF THE METALLIC  
ELEMENTS

## INTRODUCTION

THE metallic elements exhibit striking differences in physical character from the non-metallic elements. With the exception of mercury, they are all solid at ordinary temperatures, many of them are very heavy, they all possess a peculiar power of reflecting light, giving rise to the so-called metallic lustre, they are very opaque, and are better conductors of heat and electricity than the non-metals. Their chemical properties differ very widely, the most powerful combinations being formed by the metals of lowest density (sodium lithium, etc.), and the feeblest combinations by those of the greatest density (platinum, gold, etc.). An account of the occurrence and distribution of the metals in nature is given under the respective headings, as well as many of their physical and chemical properties. The following table shows the densities and melting points of the better known metals. The densities are compared with water at 15.5° as the unit :—

[TABLE

*Table showing the Densities and Melting Points of the better known Metals :—*

NAME	SPECIFIC GRAVITY	MELTING POINTS
LITHIUM	0.593	180°
POTASSIUM	0.865	62.5
SODIUM	0.974	97.6
CALCIUM	1.58	} Red heat
MAGNESIUM	1.75	
ALUMINIUM	2.56 to 2.67	} Intermediate between Zinc and Silver
ARSENIC	5.88	
ANTIMONY	6.80	Unknown
ZINC	6.86 to 7.1	425°
TIN	7.29	412°
IRON	7.79	228°
MANGANESE	8.0	1500 to 1600
COBALT	8.54	} Highest temperature of forge
CADMIUM	8.70	
NICKEL	8.8	228 to 300
COPPER	8.96	Highest temperature of forge
BISMUTH	9.90	1091
SILVER	10.50	258
LEAD	11.45	1023
MERCURY	13.59	325
GOLD	19.50	40
PLATINUM	21.50	1102
		} Temperature of oxhydrogen blow-pipe

The metals form a large class of compounds with the non-metals, in which, as a rule, the physical properties of the metals disappear. They also unite with each other to form alloys, but such compounds are, as a rule, by no means definite in their character, and in most cases do not possess any of the characteristics of true chemical combinations. The combinations of metals with mercury are termed amalgams.



The melting points of alloys are frequently lower than those of either of their constituent metals, while the specific gravity is frequently higher than the means of their constituents.

### CLASSIFICATION OF THE METALS

The division of the metals into classes, with relation to their atomicities, has been already given, and a classification on this basis is frequently adopted in modern text books. Such a classification, although showing the comparative atom replacing power of the various metals, fails to exhibit those more intimate analogies in chemical characteristics, which afford a wider basis for general discussion. The following classification groups together those metallic elements which exhibit the greatest analogy in their chemical properties and characters:—

*Group 1.*—METALS OF THE ALKALIES.—Potassium, Sodium, Lithium, Cæsium, Rubidium (Ammonium).

*Group 2.*—METALS OF THE ALKALINE EARTHS.—Calcium, Strontium, and Barium.

*Group 3.*—METALS OF THE EARTHS.—Aluminium, Yttrium, Erbium, Cerium, Lanthanium, and Didymium.

*Group 4.*—THE ZINC CLASS.—Zinc, Magnesium, Cadmium, Indium, and Beryllium or Glucinum.

*Group 5.*—THE IRON CLASS.—Iron, Manganese, Cobalt, and Nickel.

*Group 6.*—THE TIN CLASS.—Tin, Titanium, Zirconium, and Thorium.

*Group 7.*—THE CHROMIUM CLASS.—Chromium, Molybdenum, Tungsten, and Uranium.

*Group 8.*—THE ANTIMONY CLASS.—Antimony, Arsenic, Bismuth, Vanadium, Niobium, and Tantalum.

*Group 9.*—THE LEAD CLASS.—Lead and Thallium.

*Group 10.*—THE SILVER CLASS.—Silver, Mercury, and Copper.

*Group 11.*—THE GOLD CLASS.—Gold, Platinum, Palladium, Rhodium, Ruthenium, Iridium, and Osmium.

A tabular statement of the characteristics of each group will be given at the end of the description of its individual members and their compounds.

The following table gives a classification of the better known metals according to their capability of decomposing water:—

*Group 1.*—Metals which decompose water at the ordinary temperature.—Potassium, Sodium, Lithium, Cæsium, Rubidium, Calcium, Strontium, Barium.

*Group 2.*—Metals which do not decompose water at the ordinary temperature, but which effect its decomposition at a high temperature.—Aluminium, Zinc, Cadmium, Magnesium, Manganese, Cobalt, Iron, Nickel, Tin, Chromium, Bismuth.

*Group 3.*—Metals which do not decompose water either at the ordinary or at elevated temperatures.—Copper, Mercury, Silver, Gold, Platinum, Iridium.

## METALS OF THE ALKALIES

### POTASSIUM

SYMBOL, K

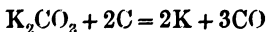
COMBINING WEIGHT, 39·1

POTASSIUM was discovered by Sir Humphrey Davy in the year 1807. He obtained it by exposing potash (potassium hydrate) to the action of a powerful galvanic current. Previous to his experiment, potash, together with soda and the alkaline earths, were regarded as elements.

**DISTRIBUTION.**—Potassium in the form of chloride is found in large beds at Stassfurt in Germany, it also occurs as chloride, bromide, and iodide, in sea water, and as nitrate in some parts of the soil of tropical

countries, principally in India. In small quantities potassium is met with in all fertile soils, its original source being the felspar of granitic rocks, which gradually undergoes decomposition by the action of the carbonic anhydride of the air in presence of moisture, potassium carbonate being formed. This salt is taken up by plants, and the potassium is found in their juices in combination with organic acids.

**PREPARATION.**—Potassium is now prepared by reducing the carbonate by carbon at a high temperature. Crude tartar or argol (acid potassium tartrate) is ignited in a covered iron crucible until it ceases to emit vapours. A black mass is thus obtained which consists of an intimate mixture of potassium carbonate and carbon. This is rapidly cooled, broken into small lumps and introduced into a wrought iron retort, which is connected with a cooled receiver. The retort and its contents are then raised to a high temperature, when the potassium distils over and is received into naphtha. Carbonic oxide is plentifully evolved during the distillation.

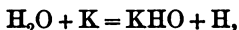


The whole process requires the greatest care, as the vapour of the metal takes fire if allowed to come into contact with air. It decomposes water, and a black explosive compound is also liable to be formed, which detonates on the slightest friction. The crude metal must be re-distilled in order to obtain it in a pure state. Potassium may also be obtained by the action of metallic iron on potash at a white heat.

**PROPERTIES.**—Potassium is a bluish white metal, of specific gravity '865, which at ordinary temperatures may be readily cut with a knife. The recently cut surface rapidly tarnishes, from the formation of the oxide  $\text{K}_2\text{O}$ . Potassium is brittle at  $0^\circ$  and melts at  $62.5$ , boiling below a full red heat. Thrown into water it decomposes it with such energy, that the



evolved hydrogen is set on fire, and burns with a purple tint, arising from the presence of a little of the vapour of the metal. The following action occurs :—

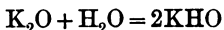


potassium hydrate being formed. Potassium is monatomic, replacing one atom of hydrogen in combination.

### PRINCIPAL COMPOUNDS

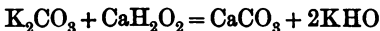
**OXIDES.**—Of these there are three, viz., the monoxide  $\text{K}_2\text{O}$ , the dioxide  $\text{K}_2\text{O}_2$ , and tetroxide  $\text{K}_2\text{O}_4$ .

**POTASSIUM MONOXIDE**,  $\text{K}_2\text{O}$ , is formed when metallic potassium is exposed to dry air,  $\text{K}_2 + \text{O} = \text{K}_2\text{O}$ . It is a white substance, fusible at a red heat; is very deliquescent, rapidly absorbing moisture from the air, and forming potassium hydrate.



The dioxide and tetroxide are produced by the action of oxygen on potassium at a high temperature.

**POTASSIUM HYDRATE**, caustic potash,  $\text{KHO}$ , is formed, as already noticed, by the action of water on the monoxide. It is prepared on a large scale by boiling a solution of potassium carbonate with slaked lime, calcium carbonate being precipitated.



The solution, after standing for some time to allow of the complete separation of the calcium carbonate, is drawn off and evaporated to dryness, and the residue fused and cast into sticks. Potassium hydrate is a white deliquescent solid, very soluble in water, and possessing powerfully alkaline properties. It is largely employed in the arts for the manufacture of soft soap, and is also extensively used as a laboratory re-agent, and to some extent in medicine as a caustic.

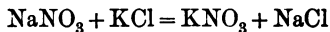
**POTASSIUM CARBONATE,  $K_2CO_3$ .**—This salt is largely prepared from wood ashes, which are brought to this country from America and Russia. The ashes are treated with water, and the clear solution, which is generally more or less brown in colour, is evaporated in iron pans. The solid product so obtained consists mainly of potassium carbonate with about twelve per cent. of sulphate and a little chloride. It is in this stage called *crude potash* or *potashes*. By calcining this crude material the water and organic substances are expelled, and a purer product left, commercially known as *pearl ash*. Pure potassium carbonate is generally prepared by calcining cream of tartar, dissolving out the carbonate from the charred mass, and evaporating the resulting solution. Potassium carbonate is a white, crystalline, deliquescent salt, which dissolves freely in water, the resulting solution having an alkaline taste and reaction. The chief use of the salt in the arts is in the manufacture of soap and glass, and for the preparation of the potassium compounds.

**HYDROGEN POTASSIUM CARBONATE.**—Bi-carbonate of potash,  $HKCO_3$ , is prepared by passing a current of carbonic anhydride through a strong solution of the preceding salt. It is white, crystallisable, and less soluble in water than potassium carbonate, and the resulting solution is very feebly alkaline. Bi-carbonate of potash is used in medicine.

**POTASSIUM NITRATE (Nitre, Saltpetre),  $KNO_3$ .**—This salt is imported in large quantities from India, where in several places it forms an efflorescence on the surface of the soil. Its production is carried on artificially in France in so-called nitre beds, consisting of heaps of earth and old mortar rubbish, which are freely exposed to the air in open sheds. The mass is periodically watered with putrid urine, the ammonia of which is gradually oxidised to nitric acid, which unites with the lime present to form calcium nitrate. This is, after a time, obtained from the mass by lixiviation, and the

solution treated with crude potassium carbonate, when calcium carbonate is precipitated, and potassium nitrate formed, which is ultimately obtained in the crystalline form by evaporation. Potassium nitrate is prepared from soils containing it by somewhat similar treatment, the crude nitre being purified by re-crystallisation.

Potassium nitrate is also prepared in large quantities by the mutual reaction of sodium nitrate and potassium chloride. When these two salts are dissolved in water in equivalent proportions, the solutions mixed, and concentrated by evaporation, sodium chloride is precipitated in small crystals, which may be removed by a perforated ladle, and potassium nitrate remains in solution, and crystallises out on the cooling of the liquid. The action which occurs is simply that of double decomposition, thus :—



This action is a good type of a class of chemical decompositions which are dependent on the different solubilities of various salts in water. It may be taken as a general rule that when two salts in solution are mixed, which are capable by mutual decomposition of producing a salt less soluble in the liquid, such a salt will be produced, and can be separated. In the action of potassium chloride and sodium nitrate the mutual decomposition is much facilitated by the fact that, while the sodium chloride formed is scarcely more soluble in hot water than in cold, the solubility of potassium nitrate is considerably increased by increase of temperature, 100 parts of *boiling* water being capable of holding 200 parts of this salt in solution, while the same quantity of *cold* water can only retain 30 parts.

Potassium nitrate crystallises in anhydrous rhombic prisms. It requires for solution about seven parts of water at 15°. It may be fused at a moderate temperature without change, forming, when cast into moulds,

the sal-prunella of the pharmacist. Exposed to a red heat, it becomes decomposed, oxygen being evolved and potassium nitrite ( $\text{KNO}_2$ ) formed. Potassium nitrate readily gives up its oxygen to combustible bodies, and is thus used very extensively for the manufacture of gunpowder and fireworks, and in the laboratory as an oxidising agent.

GUNPOWDER consists of an intimate mixture of nitre, sulphur, and charcoal, the proportions varying slightly in different countries. In England the proportions used are, nitre 75 parts, sulphur 10 parts, and charcoal 15 parts. The materials should be as pure as possible, and charcoal made from the Dogwood or Alder is preferred. The explosive effects of gunpowder are due to the respective ingredients being so proportioned that immediate and complete combustion ensues, with a large development of gas, the volume of which is considerably increased by the high temperature of the explosion. The action which occurs is the combustion of the carbon by union with the oxygen of the nitre, carbonic acid and carbonic oxide being formed, and nitrogen liberated; while the sulphur unites with the potassium to form potassium sulphide. As gunpowder contains within itself all the elements necessary for complete combustion, it can burn under water with as great facility as in the air.

POTASSIUM CHLORIDE,  $\text{KCl}$ , is found native in large beds at Stassfurt in Germany, and is also present in sea water, and is a constituent of "kelp." It is soluble in water, crystallises in cubes, and is used for the preparation of potassium compounds generally, more especially in the manufacture of potash alum, and of potassium chlorate.

POTASSIUM SULPHATE,  $\text{K}_2\text{SO}_4$ , is a white crystalline salt, not very soluble in water. It is a constituent of sea water, and is found in the ashes of land and water plants.

HYDROGEN POTASSIUM SULPHATE,  $\text{KHSO}_4$ , also called

acid potassium sulphate, is left as a residue from the preparation of nitric acid by the action of sulphuric acid on potassium nitrate. It is crystalline, and very soluble in water.

**POTASSIUM CHLORATE,  $\text{KClO}_3$ .**—The preparation of this salt, as well as of the perchlorate, has been already noticed under the head of the corresponding acids (chloric and perchloric). Instead of passing chlorine gas into a solution of potassium hydrate, potassium chlorate is more frequently prepared from a mixture of calcium hydrate and potassium chloride. By the passage of chlorine through the mixture, calcium hypochlorite is first formed, which, as the temperature rises, decomposes, calcium chlorate being formed, which reacts on the potassium chloride, with formation of potassium chlorate and calcium chloride.

Potassium chlorate crystallises in anhydrous rhomboidal tables; it is but slightly soluble in water, and, from the ease with which it parts with its oxygen, is a powerful oxidising agent. It is used as a source of oxygen, and in the manufacture of matches.

**POTASSIUM IODIDE,  $\text{KI}$ ,** crystallises in cubes, which are very soluble in water, and are also dissolved by alcohol. It is prepared by dissolving iodine in caustic potash, and evaporating the solution to dryness, and igniting the residue. It may also be prepared by digesting iodine and iron-filings together until the solution becomes colourless. Ferrous iodide is formed, and the solution, by treatment with potassium carbonate, yields ferrous carbonate as a precipitate, and potassium iodide in solution, which, on evaporation, yields crystals of iodide of potassium.

**POTASSIUM SULPHIDES.**—By passing sulphuretted hydrogen into a solution of potassium hydrate, the compound  $\text{KHS}$ , known as hydrogen potassium sulphide, or potassium sulphydrate, is formed. By fusing potassium hydrate with the proper proportions of sulphur, the compounds  $\text{K}_2\text{S}$ ,  $\text{K}_2\text{S}_2$ ,  $\text{K}_2\text{S}_3$ , and  $\text{K}_2\text{S}_5$ , may

be prepared. They are all soluble in water, and are decomposed by most acids.

**TESTS FOR THE POTASSIUM COMPOUNDS.**—Most of the potassium compounds are soluble in water, the least soluble being the acid tartrate, the perchlorate, and the double chloride of platinum and potassium. The potassium salts impart a violet colour to flame, and give a spectrum characterised by two bright lines, one in the red and one in the violet portion. A solution suspected to contain potassium may be divided into three parts. The one is heated with a caustic alkali, in order to prove the absence of salts of ammonia, which, if present, would react like potassium with the two succeeding tests. The other two portions of the solution may now be respectively treated, the one with a strong solution of tartaric acid, and the other with alcohol and solution of platinum chloride. A white crystalline precipitate in the first case, and canary-yellow crystalline one in the second, prove the presence of potassium.

## SODIUM

**SYMBOL, Na**

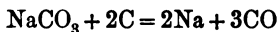
**COMBINING WEIGHT, 23**

SODIUM was discovered by Sir Humphrey Davy in the year 1807, and was obtained by him from sodium hydrate by similar means to those by which he had previously prepared potassium.

**DISTRIBUTION.**—Sodium is found in nature only in combination, its principal native compound being the chloride,  $\text{NaCl}$ , which occurs in the solid form as rock salt, and in solution in sea water. It is also met with as sodium nitrate, as silicate in many minerals, and in combination with boracic acid as borax. Sodium is a very widely diffused element, the spectroscope revealing that its presence is almost universal.

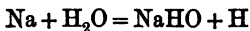
**PREPARATION.**—Sodium is now extensively manufactured on a commercial scale by reducing sodium

carbonate by means of carbon. In practice, thoroughly dried sodium carbonate is intimately mixed with a slight excess of charcoal or coal, both materials being finely powdered. The mixture is then calcined, and introduced into iron cylinders, arranged in a reverberatory furnace, and exposed to a strong heat. The following action occurs :—



The sodium distils over, and is collected in receivers, and is subsequently melted under naphtha, and cast into bars or ingots. Metallic sodium may also be obtained by the electrolysis of sodium hydrate, and by decomposing sodium hydrate at a white heat by metallic iron.

**PROPERTIES.**—Sodium has a bright metallic lustre and silver-white colour. It is soft at ordinary temperatures, and may be readily cut with a knife, the exposed surfaces, however, becoming rapidly dull from the formation of oxide. Its specific gravity is 0.97, and it melts at 97°. When heated in the air, sodium burns with a bright yellow flame. When a fragment is thrown into cold water, it decomposes the water with great energy, evolving hydrogen, sufficient heat being at the same time developed to fuse the metal, which runs about upon the surface of the water, and gradually disappears, sodium hydrate,  $\text{NaHO}$ , being formed—



If hot water is employed, the liberated hydrogen catches fire, and burns with a flame which has a yellow colour, from the presence of a little sodium vapour.

Sodium is monatomic, replacing one equivalent of hydrogen in combination. Both the metal and its salts have extensive commercial applications. Metallic sodium is extensively employed for the preparation of ~~magnesium~~ magnesium and aluminium, and, to a smaller extent, in the preparation of other less useful metals.

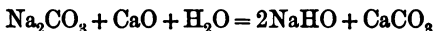
## PRINCIPAL COMPOUNDS

Two oxides of sodium are known—the monoxide,  $\text{Na}_2\text{O}$ , and the dioxide,  $\text{Na}_2\text{O}_2$ .

**SODIUM MONOXIDE,  $\text{Na}_2\text{O}$ .** may be prepared by allowing sodium to become oxidised in dry air ( $2\text{Na} + \text{O} = \text{Na}_2\text{O}$ ) or by heating sodium hydrate with sodium ( $\text{NaHO} + \text{Na} = \text{Na}_2\text{O} + \text{H}$ ). It is a yellowish white substance which absorbs moisture from the air with great rapidity, forming sodium hydrate or caustic soda,  $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaHO}$ .

**SODIUM DIOXIDE,  $\text{Na}_2\text{O}_2$ ,** is a white substance obtained by the ignition of sodium in oxygen. It is soluble in water, but the solution rapidly decomposes, evolving oxygen and leaving sodium hydrate.

**SODIUM HYDRATE,  $\text{NaHO}$ .**—Sodium hydroxide, or caustic soda, is prepared on a large scale by boiling a solution of sodium carbonate with lime, and subsequently evaporating the clear solution, the residue being generally fused and cast into sticks.



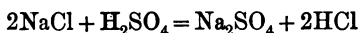
It is a white solid substance, very soluble in water, and having an intensely alkaline reaction. It is largely used in the arts in the manufacture of hard soaps, for the preparation of soluble glass, and in paper making to break down the raw fibre by boiling.

**SODIUM CHLORIDE,  $\text{NaCl}$ ,** common salt, is the most important sodium compound, inasmuch as most of the other soda salts are prepared indirectly from it. Sodium chloride is found native as rock salt, which occurs in large beds in Cheshire, and also at Cardona in Spain, at Galicia, Tyrol, various parts of America, and at many other places. Sodium chloride is also obtained by evaporating the water of certain brine springs at Droitwich and other places, and also from sea water. Rock salt is, as a rule, too impure for direct use, and is purified by solution and re-crystallisation, water being



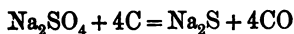
admitted to the beds, and the solution formed pumped up and concentrated in evaporating pans to obtain the crystals. Sodium chloride dissolves in about two-and-a-half parts of water, the rate of solubility being very little affected by temperature. Salt is largely employed for the preparation of sodium carbonate, for glazing stoneware, and for general domestic use.

**SODIUM CARBONATE,  $\text{Na}_2\text{CO}_3$ .** This important compound is known in its crude state as Soda Ash, and in its crystallised form as soda crystals or washing soda. It is prepared on a large scale in England from common salt, some 200,000 tons of which are consumed yearly in its manufacture. The method used is known as Leblanc's, or the salt cake process. The first stage is the conversion of the sodium chloride into sulphate. This is effected by treatment with sulphuric acid in iron pans heated by a furnace, the decomposition being completed on the hearth of the furnace. During the reaction hydrochloric acid is generated, thus :—

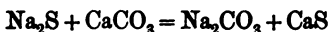


The evolved hydrochloric acid mixed with the products of combustion from the furnaces, passes to tall towers charged with coke, where a descending stream of water condenses the hydrochloric acid in order to effectually meet the requirements of the Alkali Act, which provides that at least 95 per cent. of the hydrochloric acid produced shall be removed prior to the combustion products escaping into the air.

The crude sulphate of soda, known technically as salt cake, is then ground, mixed with chalk and powdered coal, and heated on the bed of a reverberatory furnace, where the mixture melts and is well stirred. The first action which occurs is the reduction of the sodium sulphate to sulphide by the carbon of the coal, carbonic oxide being given off—



The sodium sulphide so formed then reacts with the chalk, sodium carbonate and calcium sulphide being formed, thus :—



The fused mass is raked out into a mould and allowed to cool. In this condition it is called *ball soda* or *black ash*, and contains from 20 to 30 per cent. of mixed oxide and carbonate of sodium. The next step in the process is the separation of the soda salts, which is accomplished by breaking the fused mass in pieces and lixiviating it, that is, treating it with water. The water dissolves out the sodium carbonate, and converts the sodium oxide into hydrate. The solution is allowed to settle, drawn off when clear, and evaporated in iron pans, the waste heat from the black ash furnace being used for the purpose, the residue is calcined, and then constitutes the soda ash of commerce, containing from 48 to 56 per cent. of real soda ( $\text{Na}_2\text{O}$ ) as carbonate and hydrate. The chief impurities present are small quantities of sulphate, chloride, and sulphite. In order to obtain crystals of the carbonate, the soda ash is treated with hot water, and the clear solution on standing deposits rhomboidal prisms having the composition  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . These crystals have a large sale for cleansing purposes, while the crude soda ash is extensively used for the manufacture of glass and soap, and for the preparation of the sodium compounds generally. Before the invention of the soda ash process, the chief source of the sodium carbonate of commerce was the ashes of sea plants. The plants were burned for the purpose in large quantities, and the product was known as *barilla*, and contained about 18 per cent. of carbonate. Another source was the *natron* lakes of Egypt.

Sodium carbonate has a nauseous alkaline taste. The crystals effloresce in dry air, and are soluble in about two parts of cold water. By exposure to heat

the salt melts in its water of crystallisation, then becomes anhydrous, and at a high temperature fuses.

The value of soda ash for manufacturing purposes is dependent on the amount of real soda ( $\text{Na}_2\text{O}$ ) which it contains, and which varies, as has been already mentioned, from about 48 to 56 per cent. The determination of the percentage of sodium oxide is effected by a method of analysis known as *alkalimetry*, and which depends on determining the saturating power possessed by a definite weight of the substance by means of an acid of known strength. As an

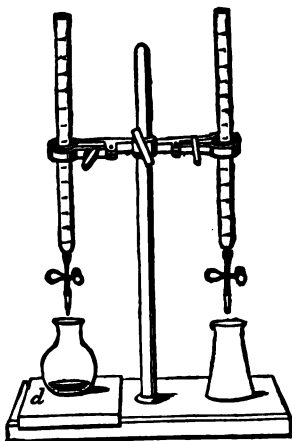
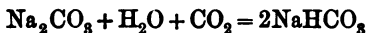


Fig. 7

example, let us assume that a solution of oxalic acid has been made by dissolving one equivalent (126 grams) of the crystallised acid,  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ , in one litre (1000 CC) of distilled water. Now, as oxalic acid is dibasic, one equivalent of the acid combines with two equivalents of a monad metal, such as sodium, to form a neutral salt. The 126 grams of  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$  will therefore saturate 62.6 grams = two equivalents of Na,

or 78.6 grams of  $\text{Na}_2\text{O}$ . The 1000 CC of the acid solution equal therefore 78.6 grams of  $\text{Na}_2\text{O}$ , and each CC will saturate  $\frac{1}{1000}$  of  $78.6 = .0786$  gram of  $\text{Na}_2\text{O}$ . Let us assume that 10 grams of a sample of soda ash have been carefully weighed, and dissolved in a little distilled water in a flask. The standard solution of oxalic acid is poured into a glass tube called a Burette or Alkalimeter, and which is graduated in CC. (See Fig. 7). A little tincture of litmus is now added to the solution of soda ash in sufficient quantity to impart a distinct blue colour, and the solution of acid is added from the burette until the colour of the alkaline solution has changed to a faint red. The solution is then heated to the boiling point to expel carbonic acid, and a little more acid added until a *permanent* red colour is obtained. The amount of acid required then represents the amount of real soda in the 10 grams of soda ash taken. Suppose, for instance, that 70 CC of the acid solution have been used, then as each CC represents .0786 gram of  $\text{Na}_2\text{O}$  the quantity of  $\text{Na}_2\text{O}$  in the 10 grams of soda ash will be  $.0786 \times 70 = 5.502$  grams or 55.0 per cent. It is obvious that by a reversal of the process, viz., by the employment of an *alkaline* solution of known strength, the determination of the strength of *acid* solutions can be made. This method of analysis is termed "Acidimetry." In the determinations of acids and alkalies by means of standard solutions of known strength, it is obvious that any acid or alkali may be employed in the preparation of the standard liquid, so long as its combining weight is known, and also the combining capacity of the substance to be estimated.

HYDROGEN SODIUM CARBONATE, Bicarbonate of Soda,  $\text{NaHCO}_3$ , is prepared by exposing sodium carbonate in the form of crystals, or in solution, to the action of carbon dioxide—



Hydrogen sodium carbonate is less soluble in water than the ordinary carbonate. Its chief use is in medicine and for the preparation of effervescing drinks. By exposure to a red heat it loses carbonic acid, and is converted into ordinary carbonate.

SODIUM SULPHATE, Glauber's Salt,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ .—The preparation of this compound in an anhydrous form has been already described under Sodium Carbonate. It is a neutral salt, crystallising in four-sided prisms, and is very soluble in water. It is chiefly used for glass making, and to a less extent in medicine.

HYDROGEN SODIUM SULPHATE,  $\text{NaHSO}_4$ .—An acid salt very soluble in water, which is left as a residue when sodium nitrate is decomposed by the action of sulphuric acid at a moderate temperature in the preparation of nitric acid.

SODIUM NITRATE,  $\text{NaNO}_3$ , a salt found in large quantities in Peru and Chili, where it forms large beds. It is very soluble in water, is deliquescent, and forms anhydrous rhomboidal crystals. It is extensively used as a manure, in the preparation of nitric acid, and for the manufacture of nitre.

Of the remaining sodium salts, the phosphate, hyposulphite, borate, silicate, and sulphide, are the most important. The first four of these have already been noticed under the respective headings of Phosphorus, Sulphur, Boron, and Silicon.

TESTS FOR THE SODIUM COMPOUNDS.—All the compounds of sodium, with the exception of the metantimoniate, are soluble in water, they impart a strong yellow colour to flame, and afford a characteristic spectrum. A solution which does not give any characteristic reaction of the presence of the heavy metals or of the alkaline earths, may contain either sodium, ammonium, or potassium, and if the characteristic tests for the two latter substances fail, sodium only can be present.

## LITHIUM

SYMBOL, LI.

COMBINING WEIGHT, 7

THIS metal was discovered by Arfvedson in 1817, and was first obtained from petalite, which is a silicate of aluminium and lithium. Lithium may be prepared by acting on the fused chloride by an electric current. It is white in colour, quickly tarnishing in the air; it melts at  $180^{\circ}$ , and its specific gravity is 0.58, being the lightest solid substance known. Lithium, although a comparatively scarce element, is very widely diffused, existing in many micas and felspars, and in minute quantities in many waters, in tobacco, in milk, and even in human blood. Lithium bears a certain resemblance to both the alkali metals and the metals of the alkaline earths. It is distinguished by the comparatively insoluble nature of its phosphate, hydrate, and carbonate, and by its affording a most characteristic spectrum exhibiting one bright crimson line.

## CÆSIUM AND RUBIDIUM

CÆ = 133

Rb = 85.4

THESE two metals were discovered by Bunsen and Kirchhoff in 1860, in the saline water of Dürkheim, but they have since been found in many other mineral waters. The discovery of both these metals was made through the agency of spectrum analysis, a means which has subsequently proved their existence in several plants and minerals. The ashes of tea, coffee, tobacco, and beetroot contain rubidium, while the metal is also present together with cæsium in lepidolite and petalite. From the small proportions in which these metals are present, even in those sources from which the largest yields may be obtained, they are comparatively scarce. One only, viz., rubidium, has been obtained in the metallic condition in a state of

purity. They much resemble each other in their properties, and both again resemble potassium, the salts of all three metals being isomorphous.

## AMMONIUM

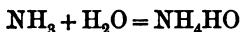
SYMBOL,  $\text{NH}_4$

COMBINING WEIGHT, 18

THE ammonium salts are presumed to contain the radical  $\text{NH}_4$ , which is termed ammonium, and which possesses to a certain extent the characteristics of a metal in forming an amalgam with mercury. By heating together mercury and sodium the two metals unite with evolution of heat and light, forming what is called sodium amalgam; and when a portion of this amalgam is placed in a solution of ammonium chloride, it swells up to a light, bulky, spongy mass, which rises to the surface of the liquid, and rapidly decomposes into ammonia, hydrogen, and mercury.

## SALTS OF AMMONIA

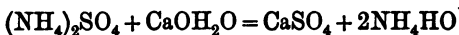
AMMONIUM HYDRATE,  $\text{NH}_4\text{HO}$ , is formed when ammonia gas is passed into water—



Its properties have been already described under the head of Ammonia.

AMMONIUM SULPHATE  $(\text{NH}_4)_2\text{SO}_4$ . This is one of the most important of the ammonium salts, and is manufactured on a large scale from the ammonia liquor of gas works. Gas liquor is a solution of sulphide and carbonate of ammonium, with a small proportion of other ammonia salts. The liquor is subjected to distillation either in boilers or in a special form of Coffey's still, and the ammoniacal vapours which are evolved, are conducted by pipes into sulphuric acid contained in a leaden vessel, called a saturator. Here the ammonia is absorbed with formation of ammonium

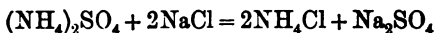
sulphate, while the carbonic acid, sulphuretted hydrogen, and steam are conducted to some condensing arrangement, in order to separate the aqueous vapour, and the gases then pass to the furnace, where the sulphuretted hydrogen is consumed, and nuisance thus avoided. The acid in the saturator is used in a concentrated condition if crystals of ammonium sulphate are required to form direct, or dilute if a solution only is needed, in which case, crystals of the salt are prepared by the subsequent evaporation of this liquid in open pans. The sulphate prepared by this means is largely used for manurial purposes, and for the preparation of other ammonia salts, and by treatment with lime for the manufacture of liquid ammonia—



In the distillation of gas liquor by the process described, only the volatile salts of ammonia, such as the sulphide and carbonate are evolved; the proportion of the ammonia which exists in the gas liquor in the form of fixed salts is comparatively small, and is frequently neglected. It can be obtained, however, by the addition of a little lime. Pure ammonium sulphate may be prepared by neutralising ammonium hydrate or carbonate with sulphuric acid. It forms long-sided prisms, which contain one equivalent of water of crystallisation, which may be expelled by heat. It is soluble in two parts of cold water.

AMMONIUM CHLORIDE,  $\text{NH}_4\text{Cl}$ , is a white crystalline salt, which is, however, generally met with in commerce in fibrous crystalline masses, which are anhydrous. It may be prepared in a pure state by neutralising ammonium hydrate or carbonate with hydrochloric acid. It is prepared in commerce by heating a mixture of ammonium sulphate and sodium chloride, when ammonium chloride sublimes and sodium sulphate remains as a residue—

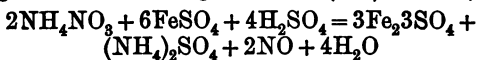




also by neutralising gas liquor with hydrochloric acid, and subsequently purifying the product by heating to expel tarry matters, and subsequently subliming the partially purified material in iron vessels covered with leaden domes.

**AMMONIUM CARBONATE**,  $(\text{NH}_4)_2\text{CO}_3$ , is a comparatively unstable salt, but the di-carbonate, as well as the so-called sesqui-carbonate, are both well-known. The sesqui-carbonate, also called hydrogen ammonium carbonate, is the carbonate of ammonia of commerce. It is prepared by subjecting a mixture of sal-ammoniac and chalk to sublimation, and is a mixture of ammonium carbonate and di-carbonate; but, according to some authorities, it consists of a mixture of di-carbonate and *carbamate*. Its formula is  $(\text{NH}_4)_4\text{H}_2(\text{CO}_3)_3$ . It is a semi-transparent salt, smelling strongly of ammonia, and which, on exposure to the air, loses water and ammonia, and becomes converted into the di-carbonate in the form of a soft white and odourless powder  $(\text{NH}_4\text{HCO}_3)$ .

**AMMONIUM NITRATE**,  $\text{NH}_4\text{NO}_3$ , may be obtained by neutralising ammonia or its carbonate with nitric acid. It is a white and slightly deliquescent salt, crystallising in six-sided prisms. Heated to  $230^\circ$  it decomposes into nitrous oxide gas and water. It is decomposed by heating with potassium hydrate, which liberates ammonia, thus,  $\text{NH}_4\text{NO}_3 + \text{KHO} = \text{KNO}_3 + \text{NH}_3 + \text{H}_2\text{O}$ . Strong sulphuric acid, on the other hand, liberates nitric acid from the compound, thus,  $2\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 + 2\text{HNO}_3$ . If heated with sulphuric acid and sulphate of iron, the nitric acid of the compound is decomposed, ferric sulphate being formed and nitrogen dioxide ( $\text{NO}$ ) evolved, thus



**AMMONIUM SULPHIDE**,  $(\text{NH}_4)_2\text{S}$ , is formed when dry

sulphuretted hydrogen is mixed with excess of gaseous ammonia at a temperature of  $-18^{\circ}$ . This compound decomposes at ordinary temperatures, losing ammonia and becoming ammonium sulphhydrate.

**AMMONIUM SULPHYDRATE**,  $\text{NH}_4\text{HS}$ , also called ammonium hydrosulphide, is prepared in solution by passing sulphuretted hydrogen gas into aqueous ammonia. The solution decomposes slowly on exposure to light, sulphur being set free, which is then dissolved by the liquid, to which it communicates a yellow colour, from the formation of ammonium disulphide  $(\text{NH}_4)_2\text{S}_2$ . Solution of ammonium sulphhydrate is largely employed as a test in the laboratory, precipitating most of the metals as sulphides from their solutions. The following are the principal metals which are not precipitated from their acid solutions by sulphuretted hydrogen, but which are thrown down as sulphides by the action of ammonium sulphhydrate. Manganese, uranium, iron, nickel, cobalt, and chromium.

Ammonia unites with several different proportions of sulphur to form a series of distinct sulphides; these different polysulphides may be obtained by distilling the corresponding sodium or potassium sulphides with an ammonia salt, such as the sulphate or chloride.

**AMMONIUM PHOSPHATES.**—These are three in number: the normal salt,  $(\text{NH}_4)_3\text{PO}_4$ , is formed when phosphoric acid is neutralised by ammonia; on drying this salt it loses ammonia, and becomes  $(\text{NH}_4)_2\text{HPO}_4$ ; and on boiling a solution of the last-named salt, the compound  $\text{NH}_4\text{H}_2\text{PO}_4$  is formed. All three salts are crystallisable, and are decomposed by exposure to a red heat, leaving a residue of metaphosphoric acid.

**TESTS FOR THE AMMONIUM SALTS.**—Nearly all the ammonium salts are soluble in water, and crystallisable; they can all either be decomposed or volatilised by heat. The ammonium salts, without exception, are decomposed by heating with caustic potash, soda, or lime, the acid

of the salt being retained by the fixed base, while ammonia is liberated in the gaseous form, and is recognised by its characteristic odour, its action on litmus paper, and the white fumes produced by the approximation of a rod moistened with hydrochloric acid. The Nessler test for ammonia has been also noticed (see Water Analysis).

The general characteristics of the alkali groups are shown in the table appended; and a further table exhibits the action of heat on the principal salts:

	HYDRATE	GENERAL CHARACTERISTICS OF SALTS	DISTINCTIVE TESTS
Potassium	Solid, white, fusible, and without odour, very soluble in water, giving an intensely alkaline solution. Colours flame violet.	Colourless, crystalline, and for the most part soluble.	With tartaric acid in excess, a white crystalline precipitate of acid potassium tartrate, which, by exposure to a continued red heat, leaves a white fusible residue of $K_2CO_3$ . With platinic chloride and alcohol, yellow crystalline precipitate of double chloride of platinum and potassium. No precipitate either with tartaric acid, or with platinic chloride.
Sodium	Resembles the potassium compound, but colours flame yellow.	Colourless, crystalline, and for the most part soluble.	Gives precipitates with excess of tartaric acid, and with platinic chloride resembling the potassium compounds. The tartaric acid compound burns entirely away at a red heat. An $NH_3$ compound, heated with a fixed alkali, evolves an odour of ammonia.
Ammonium	Gaseous, pungent odour; very soluble in water, yielding an intensely alkaline solution.	Colourless, crystalline, and for the most part soluble.	

*Table showing the Action of Heat on the Leading Compounds of the Alkali Group :—*

	POTASSIUM	SODIUM	AMMONIUM
Hydrate	Melts below redness to a clear liquid; volatilises at a full red heat.	Melts below redness, and partially volatilises at a higher temperature.	Volatilises at a comparatively low temperature.
Carbonate	Melts at a red heat; volatilises at a white heat.	Fuses at a moderate red heat.	Volatilises as above.
Bi-Carbonate	At a red heat gives off $\text{CO}_2$ and $\text{H}_2\text{O}$ , leaving $\text{K}_2\text{CO}_3$ .	At a red heat gives off $\text{CO}_2$ and $\text{H}_2\text{O}$ , and becomes $\text{Na}_2\text{CO}_3$ .	Volatilises with partial decomposition.
Sulphate	Melts at a bright red heat.	Loses all its water of crystallisation below $100^\circ$ , and melts at a red heat.	Fuses at $140^\circ$ ; is decomposed above $280^\circ$ .
Bisulphate	First gives off water, and at a red heat $\text{SO}_3$ , leaving the neutral sulphate.	Behaves like the potassium compound.	
Chloride	Melts at a low red heat; volatilises at a higher temperature.	Melts at a red heat; volatilises at a higher temperature.	Volatilises at a comparatively low temperature.
Nitrate	Melts below redness; at a red heat evolves O and becomes $\text{KNO}_2$ ; at a higher temperature gives off O and N, and becomes $\text{K}_2\text{O}$ and $\text{K}_2\text{O}_4$ .	Behaves like the Potassium compound.	Fuses at $108^\circ$ , and is decomposed between $230^\circ$ and $250^\circ$ into nitrous oxide and water.
Acid Tartrate	Is decomposed at a red heat forming a mixture of C and $\text{K}_2\text{CO}_3$ .		

## METALS OF THE ALKALINE EARTHS

## CALCIUM

SYMBOL, Ca

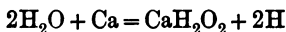
COMBINING WEIGHT, 40

THIS metal, as well as barium and strontium, was discovered by Sir Humphrey Davy in 1808, by the same means by which he had previously isolated potassium and sodium.

DISTRIBUTION. — Calcium is a very plentiful and widely diffused element, although never occurring in the free state. Its principal native compounds are the carbonate, found as chalk, marble, and limestone; the sulphate, occurring as gypsum, selenite, and alabaster; and the fluoride, constituting Derbyshire or fluor-spar.

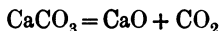
PREPARATION. — The metal may be procured by heating the iodide with sodium, or by the electrolytic decomposition of the fused chloride.

PROPERTIES. — Calcium is a metal of a light yellow colour, and of specific gravity 1.57. It easily oxidises in the air, and burns brightly when heated, forming the oxide CaO. It decomposes water at ordinary temperatures, with evolution of hydrogen and formation of calcium hydrate—



## PRINCIPAL COMPOUNDS

CALCIUM MONOXIDE (Lime), CaO, is obtained by heating the carbonate to bright redness in the air, carbonic anhydride being expelled—



The purest product is obtained from Carrara marble, and from the black marble of Derbyshire. Lime is prepared on a very large scale for commercial purposes

by heating chalk or limestone in kilns specially constructed for the purpose, various qualities of lime being made from the different sorts of native materials. Care is required in the burning, more especially if the limestone used contains alumina and silica, in which case exposure to an intense heat causes partial fusion, and the formation of silicate and aluminate of calcium, which renders the slaking of the lime difficult.

Pure calcium oxide is a white infusible solid, of specific gravity 2·3 to 3·0. When sprinkled with water, it heats, swells, and finally crumbles down to a soft, light powder. Sufficient heat is evolved in this "slaking," as it is technically termed, to char wood, the product formed being "slaked lime," or calcium hydrate,  $\text{CaH}_2\text{O}_2$ . Exposed to the air, it readily absorbs moisture and carbonic acid, eventually forming a mixture of hydrate and carbonate; and for this reason freshly-burnt lime should be carefully protected from atmospheric agencies.

Lime is used for a great variety of purposes in commerce—viz., for the preparation of bleaching powder, of sodium and potassium hydrates, for the purification of gas, the softening of water, and for the manufacture of crucibles suited to resist an intense heat. Lime is also largely employed in agriculture; mixed with the soil, it assists in the breaking up of organic substances, and in the liberation of potash from heavy clays by the decomposition of insoluble silicates.

The use of lime for making mortar is well known. A mixture of slaked lime and sand is used, and the setting and hardening are due to gradual absorption of carbonic anhydride from the air, calcium carbonate being formed, and to the formation of calcium silicate by the slow combination of the lime and sand. It is a curious fact, however, that free lime has been found in considerable quantity in the more central portions of the oldest mortars yet examined.

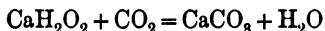
*Cements*, such as Roman, Portland, and the so-called

hydraulic lime, are all silicates and aluminates of calcium, mixed with more or less free lime. Roman cement is manufactured in this country from masses of argillaceous limestone, called "Septaria," which are found in the London clay. These are calcined at a high temperature, and subsequently ground to a fine powder. Portland cement is made in the same way, from mixtures of chalk and clay; while hydraulic lime is made from the calcination of limestones containing silica and alumina. The "setting" of cements is, no doubt, in great measure due to hydration.

CALCIUM HYDRATE,  $\text{CaH}_2\text{O}_2$ , is produced, as already described, by the action of water on calcium oxide—



It is a soft, white powder, which absorbs carbonic anhydride with great eagerness. It is very sparingly soluble in water, and is more soluble in cold than in hot water. At a temperature of  $100^\circ$ , one part of lime requires 1300 parts of water for its solution, while at  $15^\circ$ , 730 parts only are needed. A cold saturated solution of lime is known as *lime water*, and is employed as a test for carbonic anhydride, forming a precipitate of calcium carbonate—



Lime water exposed to the air soon becomes covered with a crust of calcium carbonate. Calcium hydrate is reconverted into oxide by exposure to a red heat.

CALCIUM CARBONATE (Carbonate of Lime),  $\text{CaCO}_3$ .—This compound occurs native in immense quantities, of which the chains of limestone mountains and chalk hills, and the large masses of coral reefs, may be taken as typical examples. Calcium carbonate occurs also in a semi-crystalline condition in marble, and in two well-defined crystalline forms, viz., Calc spar and Iceland spar, the crystals of both of which are rhombohedra, and as Arragonite, the crystals of which are prismatic.



Calcium carbonate is thus dimorphous. The ordinary limestones, as well as most of the native varieties of calcium carbonate, are not entirely pure, but usually contain more or less clay, oxide of iron, and sometimes organic matter. Calcium carbonate is quite insoluble in pure water, but is dissolved to a small extent by water containing carbonic acid. This may be well illustrated by passing a current of carbonic anhydride into lime water, which at first occasions a precipitate of calcium carbonate; after a time, however, this precipitate disappears, being dissolved by the excess of carbonic acid. It is by reason of this circumstance that natural waters are found to contain calcium carbonate in solution. It is also to the same cause that the formation of caverns in the mountain limestone hung with stalactites is due. Water holding in solution carbonic acid gradually dissolves away large masses of the mountain limestone, leaving corresponding cavities. From the roofs of these cavities is constantly dripping water saturated with the calcium carbonate it has dissolved from the superincumbent strata; and as the water slowly falls it parts with a portion of its contained carbonic acid by evaporation, and deposits a corresponding portion of its dissolved lime. This process, gradually going on for long periods of time, gives rise to the formation of hanging masses of calcium carbonate termed stalactites. The water which drips from these is still charged with lime, a great part of which is deposited on the floor of the cavern, forming masses called stalagmites. Occasionally, by the continual elongation of the stalactite, and upward increase of the stalagmite, the two meet, and a solid pillar is formed. The relation of calcium carbonate to the hardness of water has been already pointed out. Calcium carbonate is readily decomposed by acids, carbonic anhydride being evolved, and a corresponding lime salt formed.

CALCIUM SULPHATE,  $\text{CaSO}_4$ , occurs native in the

hydrated form in large quantities as gypsum and alabaster, and crystallised as selenite. It is precipitated whenever sulphuric acid or a soluble sulphate is added to a solution of a lime salt. It is soluble in about 500 parts of cold water, and its presence in natural waters gives rise to permanent hardness. Gypsum, when exposed to a moderate temperature, loses two equivalents of water, and becomes anhydrous. In this condition it forms the well-known *Plaster of Paris*, so much used for moulding and casting. The setting of the powder, on being mixed with water, is due to hydration, the original two molecules of water being taken up. If the gypsum is overheated, this hydration and subsequent setting does not occur, and the material is said to be overburnt.

CALCIUM CHLORIDE,  $\text{CaCl}_2$ , is formed when the hydrate or carbonate is treated with hydrochloric acid, and is a residual product in many manufacturing operations. It is a very soluble salt, containing in the crystallised state six equivalents of water: four of these equivalents may be expelled at a moderate heat, leaving a porous mass, which absorbs moisture with great avidity, and is used for the desiccation of gases. Exposed to a higher temperature, the whole of the water is expelled, and the salt fused.

CALCIUM HYPOCHLORITE,  $\text{CaCl}_2\text{O}_2$ , is the basis of the bleaching powder familiarly known as *chloride of lime*. Its preparation and bleaching action have been described under hypochlorous acid.

CALCIUM FLUORIDE,  $\text{CaF}_2$ , is found native as fluor spar in the lead mines of Derbyshire, Cornwall, and Cumberland. It is almost insoluble in water, and fuses at a high temperature. It is used for the preparation of hydrofluoric acid, and as a flux in smelting operations.

CALCIUM PHOSPHATE,  $\text{Ca}_3\text{2PO}_4$ , occurs native as apatite, and is the principal constituent of bones. It has been already noticed under phosphoric acid. Be-

sides the salts which have been described, calcium forms a nitrate,  $\text{Ca}(\text{NO}_3)_2$ , very soluble in water, a monosulphide,  $\text{CaS}$ , insoluble, and a pentasulphide, soluble.

**TESTS FOR THE CALCIUM COMPOUNDS.**—The calcium salts are distinguished from those of the preceding group by the insolubility of the carbonate and phosphate, and the comparative insolubility of the hydrate. The remaining salts are soluble. The calcium salts in neutral solutions give a white precipitate with ammonium oxalate, soluble in dilute mineral acids, but insoluble in acetic acid. The solutions likewise give (except when in an exceedingly dilute condition) a white precipitate with dilute sulphuric acid and soluble sulphates. The calcium compounds colour flame brick-red, and the spectrum is chiefly marked by the presence of a bright orange line, and a broad green one.

## BARIUM

SYMBOL, Ba                      COMBINING WEIGHT, 137

**DISTRIBUTION.**—Barium is found in the combined state in nature in considerable quantity as the sulphate, or heavy spar, and as the carbonate, or witherite.

**PREPARATION.**—Barium may be prepared by the electrolytic decomposition of the fused chloride, by passing sodium vapour over the strongly heated oxide, or by the action of sodium amalgam on a solution of baric chloride, and the subsequent distillation of the resulting barium amalgam.

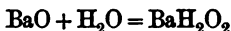
**PROPERTIES.**—Barium is a metal of a white or yellowish colour. It rapidly oxidises in the air, forming barium oxide, and decomposes water at ordinary temperatures, forming barium hydrate and free hydrogen.

## PRINCIPAL COMPOUNDS

**BARIUM OXIDE (Baryta),  $\text{BaO}$ ,** is best prepared by igniting the nitrate—



Barium oxide, as thus prepared, is a greyish porous mass, which fuses at a high temperature, and which, by treatment with water, forms barium hydrate, with evolution of heat—

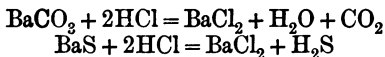


BARIUM DIOXIDE,  $\text{BaO}_2$ , is produced when baryta is gently heated in a current of oxygen. At a higher temperature, the absorbed oxygen is given off, and ordinary baryta left. Barium dioxide is a white powder, insoluble in water, and decomposed by acids.

A process for preparing oxygen from the air, by the alternate absorption and evolution of oxygen by heated barium oxide, has been tried, but was not found to be practically successful.

BARIUM HYDRATE,  $\text{BaH}_2\text{O}_2$ .—The formation of this compound, from the action of water on barium oxide and metallic barium, has been already noticed. Crystallised from a supersaturated solution, it forms crystals containing eight equivalents of water, and which are efflorescent. Barium hydrate is soluble in twenty parts of water at  $15^\circ$ , forming an alkaline solution which rapidly absorbs carbonic acid from the air, becoming covered with a crust of barium carbonate,  $\text{BaCO}_3$ .

BARIUM CHLORIDE,  $\text{BaCl}_2$ , may be prepared by dissolving the carbonate or sulphide in hydrochloric acid—



It is soluble in about two-and-a-half parts of water at  $15^\circ$ , and crystallises in flat tables, containing two equivalents of water.

BARIUM SULPHATE,  $\text{BaSO}_4$ , found native as heavy spar, is produced in the form of a white powder insoluble in water and acids when sulphuric acid or a solution of any soluble sulphate is added to a solution of a barium salt. The native compound is used for the preparation

of other barium salts, for which purpose it is ground to powder, and heated with carbon, when barium sulphide is formed, which, on the addition of an acid, yields a corresponding salt with evolution of sulphuretted hydrogen. The native sulphate is used as a permanent white paint, for which purpose it is superior to white lead in not discoloring in a foul atmosphere, but is inferior in covering power. It is also used as an adulterant of white lead.

**BARIUM CARBONATE**,  $\text{BaCO}_3$ , occurring native as *Witherite*, is produced as an insoluble white powder, on the addition of a soluble carbonate to a solution of a barium salt.

**BARIUM NITRATE**,  $\text{Ba}_2\text{NO}_3$ .—A soluble salt, prepared by dissolving the native carbonate in nitric acid. It is soluble in about eight parts of cold water, and crystallises in octahedra. It is used in pyrotechny for the preparation of green fire. Barium also forms a sulphide,  $\text{BaS}$ , and a sulphhydrate,  $\text{BaH}_2\text{S}_2$ , both soluble in water, and a phosphate, which is insoluble.

### TESTS FOR BARIUM

Barium is chiefly distinguished from calcium by the solubility of its hydrate, and the absolute insolubility of its sulphate. Barium also forms an insoluble silicofluoride and hyposulphite, the corresponding compounds of calcium and strontium being soluble. A further distinction is observed in the fact that the chloride and nitrate of Barium are permanent in the air, and not deliquescent as is the case with the corresponding compounds of calcium. Barium colours flame green, and its spectrum is characterised by several green bands.

### STRONTIUM

SYMBOL, *Sr*

COMBINING WEIGHT, 87.5.

**DISTRIBUTION**—Strontium is a less abundant element than barium. Its principal native compounds are

the sulphate, termed *Celestine*, and the carbonate or *Strontianite*.

**PREPARATION.**—Strontium is prepared in a way similar to barium.

**PROPERTIES.**—The metal has a yellow colour like calcium, decomposes water at ordinary temperatures, forming the hydrate and evolving hydrogen, and rapidly oxidises when exposed to the air forming the oxide  $\text{SrO}$ .

### PRINCIPAL COMPOUNDS

**STRONTIUM OXIDE**,  $\text{SrO}$ , is formed by igniting the nitrate; the reaction is the same as that which occurs in the preparation of barium oxide from the nitrate, and the oxide formed is similar to barium oxide in its properties.

**STRONTIUM HYDRATE**,  $\text{SrH}_2\text{O}_2$ , is formed by the action of water on the oxide, much heat being evolved. It is soluble in water, and crystallises in needles which have the composition,  $\text{SrH}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ , and are deliquescent.

**STRONTIUM CARBONATE**,  $\text{SrCO}_3$ , and Strontium sulphate,  $\text{SrSO}_4$ , may be prepared in the same way as the corresponding barium compounds, which they resemble in properties, with the exception that they are to a slight extent soluble in water. The nitrate,  $\text{Sr}_2\text{NO}_3$ , and the chloride,  $\text{SrCl}_2$ , are soluble deliquescent salts, and are respectively prepared by treating the native carbonate with nitric and hydrochloric acid. They are used in pyrotechny for the preparation of crimson fire.

### TESTS FOR STRONTIUM

Strontium in solution is distinguished from barium by giving no immediate precipitate with a solution of calcium sulphate, but affording one after standing some time. It also gives no precipitate with a soluble hyposulphite or with fluosilicic acid, and it imparts a crimson colour to flame. It gives several bands in the red, and one in the blue portion of the spectrum.

*Table showing the General Characteristics of the Compounds of the Metals of the Alkaline Earth Group, their Chief Points of Resemblance and Dissimilarity, and their Distinctive Tests :*

	OXIDE	CARBONATE	SULPHATE	CHLORIDE AND NITRATE	DISTINCTIVE TESTS
Calcium	White infusible powder uniting with water, with great evolution of heat, to form a hydrate. Soluble in 730 parts of cold water.	White and Insoluble	Soluble in 500 parts of cold water	Soluble and deliquescent	A solution of a calcium salt gives no precipitate with a soluble hyposulphite, with fluosilicic acid, or with a solution of calcium sulphate. Calcium salts impart a brick-red colour to flame.
Barium	White infusible powder, uniting with water, with great evolution of heat, to form a hydrate, freely soluble in water.	White and Insoluble	Insoluble in water and acids	Soluble and not deliquescent	Barium in solution gives an immediate precipitate (white) with solution of calcium sulphate, and also gives white precipitates with fluosilicic acid and sodium hyposulphite. Barium compounds impart a green colour to flame.
Strontium	Resembles the preceding compound.	White and Insoluble	Almost Insoluble in water	Soluble and deliquescent	Strontium in solution does not give an immediate precipitate with solution of calcium sulphate, but a precipitate is formed after some time. Strontium salts do not give precipitates with either fluosilicic acid or a soluble hyposulphite. They colour flame crimson.

*Table showing the Action of Heat on the Leading Compounds of the Alkaline Earth Group:—*

	HYDRATE	CARBONATE	SULPHATE	CHLORIDE	NITRATE
Calcium	Loses water at a full red heat being converted into the oxide $\text{CaH}_2\text{O}_2 = \text{CaO} + \text{H}_2\text{O}$ .	Loses carbon dioxide at a full red heat in an open vessel, leaving the oxide CaO.	Melts at a full red heat without decomposition.	The crystallised salt loses the whole of its water at 200°, fuses at a low red heat, and is partially decomposed at a higher temperature.	May be heated to incipient fusion without decomposition, but at a high temperature is decomposed, evolving O and $\text{N}_2\text{O}$ , and leaving CaO.
Barium	Is acted on in a similar way to the calcium compound.	Is not decomposed by exposure to a strong red heat, but evolves $\text{CO}_2$ at a white heat, and leaves the oxide BaO.	Unaffected at a full red heat.	Loses its water of crystallisation at 100°, and melts at a full red heat.	Melts at a comparatively low temperature and decomposes at a red heat, evolving O, N and $\text{N}_2\text{O}$ , and leaving BaO.
Strontium	Is acted on in a similar way to the calcium compound.	Evolves $\text{CO}_2$ at a high temperature and leaves the oxide SrO.	Melts to a vitreous mass at a strong red heat, but is chemically unchanged.	Loses its water of crystallisation, and fuses at a red heat.	Behaves in a similar way to the barium compound.



## METALS OF THE EARTHS

## ALUMINIUM

SYMBOL, Al

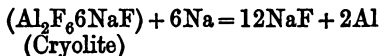
COMBINING WEIGHT, 27.5

This metal was discovered by Wohler in 1828, and was first prepared by him by decomposing aluminium chloride by metallic potassium.

**DISTRIBUTION.**—Aluminium in the combined state is a very widely diffused and abundant element. It is found as silicate in clay and shale, Fuller's earth, kaolin, felspar, and a variety of other minerals. Some precious stones, such as the ruby and sapphire, consist of aluminium in combination with oxygen as alumina. Corundum has a similar composition.

**PREPARATION.**—Aluminium may be obtained by passing the vapour of aluminium chloride over heated metallic sodium, but with greater economy and facility by the action of sodium on cryolite.

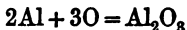
Cryolite is a double fluoride of aluminium and sodium, it is pulverised, mixed with half its weight of common salt, and the mixture arranged in a crucible in alternate layers with sodium. The mass is then rapidly heated, stirred with an iron rod, and allowed to cool, when the metallic aluminium is found in large globules. The following reaction takes place :—



This method is now carried out on a manufacturing scale.

**PROPERTIES.**—Aluminium is a silver white metal, which has a specific gravity of 2.6, and which from its lightness and malleability admits of many useful appli-

cations in the arts. It is permanent in the air, but burns when heated to redness, forming the oxide  $\text{Al}_2\text{O}_3$ —



Aluminium does not decompose water at ordinary temperatures, but is acted on by acids and by solution of potassium or sodium hydrate, an aluminate being formed and hydrogen set free. Aluminium is used for the preparation of the so-called aluminium bronze or aluminium gold, an alloy of 10 parts of aluminium with 90 parts of copper. It is also used for ornamental purposes.

### PRINCIPAL COMPOUNDS

**ALUMINIUM OXIDE, ALUMINA,  $\text{Al}_2\text{O}_3$ ,** is found native as corundum, ruby, and sapphire, and in an impure state as emery. It may be prepared by adding ammonia to a solution of an aluminium salt, and washing, drying and igniting the resulting gelatinous precipitate. As thus produced, alumina is a white powder, requiring very prolonged heating with strong acids to bring it into solution. It is only fusible at the temperature of the oxyhydrogen blow-pipe.

**ALUMINIUM HYDRATE,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .**—Occurs native as *Diaspore* and *Gibbsite*. It may be prepared by the addition of ammonia or potash to a solution of an alumina salt, such as the sulphate—



Aluminium hydrate is semi-transparent and gelatinous, easily soluble in acids and in solution of potassium or sodium hydrate. It is extensively used as a mordant in dyeing and calico-printing, from the property which it possesses of forming insoluble compounds (called lakes) with organic colouring matters. Colours capable

of fixation by this treatment are called *fast*, from the circumstance of their being so fixed on the stuff as to enable it to bear washing. Alumina is a weak base, its salts having an acid reaction.

**ALUMINIUM SULPHATE,  $\text{Al}_2\text{SO}_4$ .**—This compound is manufactured on a large scale by treating clay with sulphuric acid, and also by the treatment of certain aluminous shales containing iron pyrites. These are submitted to slow combustion in large heaps, when the sulphur is oxidised to sulphuric acid, and unites with the alumina to form aluminium sulphate, which is dissolved out of the mass by lixiviation. Aluminium sulphate is white and crystallisable, its solution being distinctly acid. Its most striking property is that of uniting with several other sulphates to form compound salts called alums, of which potash alum,  $\text{Al}_2\text{K}_2\text{4SO}_4 + 24\text{H}_2\text{O}$ , and ammonia alum,  $\text{Al}_2(\text{NH}_4)_2\text{4SO}_4 + 24\text{H}_2\text{O}$ , are the most important. They both crystallise in regular octahedra, and are manufactured on a large scale for commercial purposes. They are prepared from the aluminous shales containing sulphur, which have been already spoken of. The solution obtained from the calcination and lixiviation of these shales is mixed with potassium chloride, or the ammoniacal liquor of gas works, and the crystallised potash, or ammonia alum obtained by evaporation. Potash alum when heated melts in its water of crystallisation, and on continued exposure to heat dries up to a white porous mass, known as *burnt alum*. The chief use of alum is as a mordant. If a solution of alum is treated with sodium carbonate, as long as the precipitate which is produced is re-dissolved, a portion of the sulphuric acid previously in combination with the aluminium unites with the soda, and a *basic* aluminium sulphate, having the composition  $\text{Al}_2\text{O}_3\text{SO}_3$ , is left. This basic salt is readily decomposed, yielding up a portion of its alumina, and becoming converted into ordinary aluminium sulphate,  $\text{Al}_2\text{SO}_4$ , or  $\text{Al}_2\text{O}_3\text{3SO}_3$ , as it may be

written. This decomposition takes place when the solution is boiled, thus:—



It is also effected by the introduction of any fabric, such as calico, into the solution, the alumina being deposited in the fibres of the material, which is then capable of acting as a mordant to attract and fix organic colouring matter. The term “alum” has been extended to other compound salts in which the isomorphous oxides of iron, chromium, and manganese are substituted for alumina. The characteristics of all these so-called alums are that they have a similar constitution, contain twenty-four equivalents of water of crystallisation, and crystallise in the same form; they are thus, when mixed, incapable of separation by crystallisation.

ALUMINIUM CHLORIDE,  $\text{Al}_2\text{Cl}_6$ , is obtained by heating a mixture of alumina and charcoal in a current of chlorine. It is a white volatile deliquescent solid.

ALUMINIUM SILICATES.—These constitute a very important class of native compounds, of which ordinary clay has the largest commercial applications. Clays are of very varying degrees of purity, the chief impurities being lime and oxide of iron. Those containing much carbonate of lime, known by their effervescence with acids, are called marls. The chief use of clays is in the manufacture of earthenware and porcelain. For this purpose the clay is ground, mixed with water, the coarser particles allowed to settle, and the water containing the finer portions run off into a separate vessel where the finely divided clay subsides. The coarser articles of earthenware, as well as those specially intended to be of a porous nature, are made of the unmixed clay, the common coloured varieties generally answering the purpose.

For china and porcelain, a white clay called china clay, which is a product arising from the decomposition of felspar, is used. The articles are manufactured from

the pure clay and are subsequently dipped into a vessel containing water in which is suspended a glazing material, finely powdered felspar being frequently employed. In the subsequent *firing* of the ware, as the baking process is termed, the felspar fuses and gives a glaze to the articles, improving their appearance and rendering them impervious to liquids. A coarser glazing for commoner earthenware articles is procured by throwing common salt into the furnaces where the *firing* is being carried out, the sodium chloride volatilises, the sodium uniting with the silica of the ware forming a fusible sodium silicate, while hydrochloric acid escapes.

The other members of the group of the metals of the earths are too rare to merit attention in the present book.

#### TESTS FOR ALUMINIUM

The alumina salts are colourless, and with ammonia yield a white gelatinous precipitate of aluminium hydrate insoluble in excess of the reagent. The fixed caustic alkalis produce the same precipitate, easily soluble in an excess of the alkali. Aluminium is distinguished from the preceding groups by yielding a soluble sulphate, insoluble hydrate, and producing no carbonate. When a salt of aluminium is moistened with a solution of cobalt and exposed to the blow-pipe flame, it assumes a blue colour.

*The following Table shows the Action of Heat on the most important Aluminium Compounds :—*

Hydrate	Chloride	Sulphate	Potash Alum	Ammonia Alum
Parts with its water at a strong red heat and becomes $\text{Al}_2\text{O}_3$	The anhydrous salt is entirely volatilised at a red heat. The hydrated salt is at the same temperature decomposed into alumina and hydrochloric acid.	Melts in its water of crystallisation, then swells up to a porous mass of anhydrous salt; at a red heat, is decomposed, $\text{SO}_3$ passing off, and $\text{Al}_2\text{O}_3$ being left.	Fuses in its water of crystallisation, and becomes anhydrous at $200^\circ$ , at a very high temperature is decomposed, $\text{SO}_3$ being given off.	Fuses in its water of crystallisation and at a red heat is decomposed losing its ammonia and $\text{SO}_3$ , and leaving $\text{Al}_2\text{O}_3$

## THE ZINC GROUP

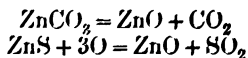
### ZINC

SYMBOL, Zn

COMBINING WEIGHT, 65

**DISTRIBUTION.**—Zinc is a moderately abundant metal, of which the principal ores are Calamine, which is a Carbonate, Blende, also called Black Jack, which consists of sulphide, and the red oxide. The chief places furnishing zinc ores are Silesia, Belgium, Poland, and England.

**PREPARATION.**—The first step in the treatment of zinc ore is calcination, by which the carbonate and sulphide are both converted into oxide.



The calcined ore is then mixed with ground coal or coke and subjected to distillation, the zinc passing over

and being received in water ( $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ ). The metal so obtained is then melted and cast into ingots.

**PROPERTIES.**—Zinc is a metal of a bluish white colour, and having a specific gravity of 6·8 to 7·2. At ordinary temperatures it is brittle and exhibits a crystalline fracture when broken. If heated to about  $130^{\circ}$  it becomes malleable and can be rolled into sheets, while exposed to a temperature of about  $200^{\circ}$  it is so brittle that it can be easily reduced to powder in a mortar. It melts at a low red heat, and may be distilled at a higher temperature. When strongly heated in contact with air it takes fire, burning with a brilliant light, and forming the oxide  $\text{ZnO}$ . Zinc is not perceptibly oxidised in the air, and is hence used for coating more oxidisable metals, such as iron, which is then said to be galvanised. Zinc is attacked by boiling water to a slight extent, hydrogen being evolved, and is rapidly attacked and dissolved by acids, a salt being formed and hydrogen given off. The metal is largely used in the sheet form for roofing. It generally forms the positive element in galvanic batteries, and is employed for the manufacture of brass. The salts of zinc are colourless. Commercial zinc generally contains small quantities of lead, and iron, and traces of tin, cadmium, and sometimes arsenic as impurities.

#### PRINCIPAL COMPOUNDS

**ZINC OXIDE,  $\text{ZnO}$ ,** occurs native as “red oxide of zinc,” the colour being due to the presence of the oxides of iron and manganese. Zinc oxide may be obtained by burning the metal in air or in the hydrated form by precipitating a solution of one of the zinc salts with a fixed alkali. It forms a fine white powder, which changes its colour to yellow on heating to low redness, becoming white again on cooling. It is insoluble in water, but soluble in acids, with which it forms salts. It is used as a paint, having the advantage over lead

pigments in not blackening by the action of sulphuretted hydrogen.

**ZINC SULPHATE**,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$  (also called white vitriol), is a soluble salt isomorphous with magnesium sulphate. It is left as a residue from the preparation of hydrogen by the action of sulphuric acid on metallic zinc. The crystals are efflorescent, and by exposure to a moderate temperature lose six equivalents of water, and at a higher temperature the remaining equivalent is given off.

**ZINC CHLORIDE**,  $\text{ZnCl}_2$ , is a very soluble deliquescent substance produced by heating zinc in chlorine, or by dissolving the metal in hydrochloric acid. Its solution possesses antiseptic properties, and is sold under the title of "Burnett's Disinfecting Fluid."

**ZINC CARBONATE**,  $\text{ZnCO}_3$ , occurs in nature as Calamine, and is produced as a white precipitate when an alkaline carbonate is added to a solution of a zinc salt. The precipitate so obtained, however, always contains hydrated oxide. Zinc carbonate is decomposed by a red heat,  $\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2$ .

**ZINC SULPHIDE**,  $\text{ZnS}$ , occurring native as zinc-blende, is produced artificially as a white gelatinous precipitate by adding an alkaline sulphide to a zinc solution. Zinc sulphide is soluble in mineral acids, but insoluble in acetic acid.

#### TESTS FOR ZINC

Zinc in solution may be identified by the production of a white sulphide on the addition of a solution of an alkaline sulphide and by the formation of white hydrated oxide on the addition of an alkali, soluble in ammonia. Before the blow-pipe on charcoal, with a little cobalt chloride the zinc compounds give a green coloured mass.



## CADMIUM

SYMBOL, Cd

COMBINING WEIGHT, 112

**DISTRIBUTION.**—Cadmium is a comparatively rare metal occurring in many zinc ores, and in combination with sulphur forming the mineral Greenockite.

**PREPARATION.**—Metallic Cadmium is obtained from zinc ores by the same process by which the zinc is extracted, but owing to its volatility it distils over first.

**PROPERTIES.**—Cadmium is a soft ductile metal of a white colour, and much resembling zinc in its general appearance. Heated in contact with the air it burns, forming the oxide  $\text{CdO}$ . It is dissolved freely by nitric acid, and is also dissolved by hot sulphuric and hydrochloric acids. The metal is sometimes employed for making fusible alloys, one of which, consisting of lead, bismuth, tin, and cadmium, melts at  $60^\circ$ .

## PRINCIPAL COMPOUNDS

Cadmium forms one oxide,  $\text{CdO}$ , a brown infusible powder, which is produced when the metal burns in air or by the ignition of the carbonate or nitrate. The sulphate  $\text{CdSO}_4$ , chloride  $\text{CdCl}_2$ , and nitrate  $\text{Cd}(\text{NO}_3)_2$  are all soluble salts produced by the action of the corresponding acids on the oxide, the carbonate, or the metal. Cadmium sulphide,  $\text{CdS}$ , is a yellow insoluble powder precipitated by sulphuretted hydrogen from any solution containing the metal. It is used as a paint. Cadmium iodide is used in photography.

## TESTS FOR CADMIUM

Cadmium in solution may be identified by the production of a yellow insoluble sulphide by the action of sulphuretted hydrogen or an alkaline sulphide. The only other yellow sulphide is that of arsenic which is

freely dissolved by alkaline sulphides. Before the blow-pipe and charcoal the cadmium compounds are reduced, and the metal oxidised, forming a brown incrustation of the oxide.

## MAGNESIUM

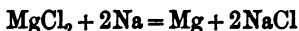
SYMBOL, Mg

COMBINING WEIGHT, 24

Magnesium was first isolated by Bussey in 1829, but its existence was previously established by Davy in 1809.

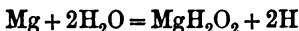
**DISTRIBUTION.**—The native compounds of magnesium are found in considerable quantity in various localities. The carbonate occurs mixed with that of calcium in magnesian limestone, or Dolomite, while the silicate occurs as Steatite, Soapstone, Talc, Asbestos, Amianthus, and Meerschaum. Magnesium also occurs as sulphate, in sea water, and in many mineral waters.

**PREPARATION.**—Magnesium may be prepared by the electrolytic decomposition of the fused chloride, but is more commonly prepared by heating the chloride with metallic sodium—



The operation is generally conducted in a clay crucible, the fused mass being stirred with an iron rod to effect the union of the metallic globules. Large quantities of magnesium are now prepared by this process.

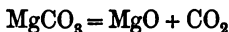
**PROPERTIES.**—Magnesium is a silver white metal of specific gravity 1.75, retaining its lustre in dry air, but becoming slowly oxidised in the presence of moisture. It is very slowly acted on by cold water, but more quickly by boiling water, hydrogen being liberated and magnesium hydrate formed—



Magnesium fuses at about the same temperature as zinc, and may be distilled in an atmosphere of hydrogen at a full red heat. It is capable of being drawn, rolled, and cast. Heated in the air it burns with a dazzling bluish white light, forming the oxide, Magnesia ( $\text{Mg} + \text{O} = \text{MgO}$ ). The light emitted by burning magnesium is very rich in actinic rays, and is hence of great use in photography. Magnesium is one of the few elements that unite directly with nitrogen at a high temperature.

### PRINCIPAL COMPOUNDS

**MAGNESIUM OXIDE.**—Magnesia,  $\text{MgO}$ , is formed when magnesium burns in the air. It is generally obtained by exposing the carbonate to a red heat—



It may also be prepared from the nitrate in a similar way. The oxide prepared from the ignition of the carbonate constitutes the *calcined magnesia* of pharmacy. It is a soft white powder, which is tasteless and infusible. It has an alkaline reaction, is to a very slight degree soluble in water, and when mixed with water forms the hydrate  $\text{MgH}_2\text{O}_2$  without evolution of heat. The hydrate is found in nature in a crystalline form as *Brucite*.

**MAGNESIUM CARBONATE**,  $\text{MgCO}_3$ , occurs in nature as a crystallised mineral, *Magnesite*, and is a constituent of magnesian limestone. The pure carbonate cannot be prepared by the action of an alkaline carbonate on a soluble magnesium salt, as a mixture of carbonate and hydrate is precipitated under these conditions. If, however, the mixed precipitate is suspended in water, and a current of carbonic anhydride passed, the liquid becomes clear, and on evaporation magnesium carbonate is deposited as a crystalline powder. The *magnesia alba* of pharmacy is obtained by precipitating a hot

solution of magnesium sulphate with sodium carbonate and washing the resulting precipitate. It is a mixture of hydrate and carbonate.

**MAGNESIUM SULPHATE.** — Epsom salts,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , obtains its commoner synonym from the fact of its occurrence in a mineral spring at Epsom; it is also found in many other mineral waters. It is prepared on a large scale by the action of dilute sulphuric acid on magnesian limestone, insoluble calcium sulphate and soluble magnesium sulphate being produced simultaneously. Magnesium sulphate is soluble in about three parts of water at ordinary temperatures, and the solution has a bitter taste. The salt crystallises in rhombic prisms, and is used in medicine.

**MAGNESIUM CHLORIDE**,  $\text{MgCl}_2$ , is also a constituent of some mineral waters. It can be prepared in solution by dissolving ordinary magnesia alba in hydrochloric acid, but on evaporating the solution to dryness, the salt is decomposed, hydrochloric acid being evolved and magnesia left. By the addition of ammonium chloride, this decomposition may be prevented, and on evaporation and fusion, the ammonium chloride is volatilised, and magnesium chloride left.

Of the remaining salts of magnesia, the nitrate,  $\text{Mg}_2\text{NO}_3$ , and the ammonia-phosphate,  $\text{Mg}.\text{NH}_4\text{PO}_4 + 6\text{H}_2\text{O}$ , are the most important. The former is obtained by dissolving magnesia in nitric acid, and is very soluble, the latter is almost insoluble, and is produced as a crystalline precipitate on adding ammonia and sodium phosphate to a solution of a magnesium salt.

#### TESTS FOR MAGNESIUM

The salts of magnesium are soluble with the exception of the carbonate and ammonia-phosphate. Magnesium is distinguished from the other members of the group to which it belongs by not forming a sulphide when in aqueous solution, and by the solubility of its carbonate in ammonium chloride.

## BERYLLIUM

SYMBOL, Be

COMBINING WEIGHT, 9·8

BERYLLIUM, sometimes called Glucinum, is an exceedingly rare metal, found in combination with silica and alumina as the mineral beryl, and in combination with alumina as chrysoberyl. It may be obtained by reducing the chloride with sodium. Beryllium is a white metal of specific gravity 2·1, and is very malleable. It is dissolved freely by sulphuric and hydrochloric acids, but is very little acted on by nitric acid. It forms one oxide,  $\text{BeO}$ , and a series of salts which are soluble, colourless, and possess a sweetish taste from which characteristic the name Glucinum is derived.

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## GENERAL CHARACTERISTICS OF THE ZINC GROUP

The metals of this group do not decompose water except at elevated temperatures. The individual members vary somewhat in their characteristics. Zinc and cadmium give insoluble and characteristic sulphides, the hydrates and carbonates are insoluble, and the sulphates and chlorides soluble.

Magnesium was formerly grouped with barium, calcium, and strontium, but is more allied to zinc, not only in its character as a metal, but in its forming a volatile chloride, a soluble sulphate, and in the isomorphism of several of the compounds of the two metals.

The two following tables show the chief characteristics of the compounds of the zinc group, and the action of heat upon them :—

[TABLE

*Table showing the Action of Heat on the Principal Compounds of the Metals of the Zinc Group:—*

	OXIDE	SULPHIDE	CARBONATE	SULPHATE	CHLORIDE
Magnesium	Not affected by any temperature less than that of the oxyhydrogen blow-pipe, by which it is fused.		Is converted into MgO at a full red heat, CO <sub>2</sub> being evolved.	Melts in its water of crystallisation, and becomes solid and anhydrous at 200°. Again melts at a red heat, and is partly decomposed at a very high temperature.	The anhydrous salt melts at a low red heat without change, but if water is present, decomposition ensues, HCl passing off, and MgO being left.
Zinc	Turns yellow, but resumes its white colour on cooling.	Melts at a high temperature, and in a current of air becomes ZnO, the S passing off as SO <sub>2</sub> .	Becomes ZnO, and evolves CO <sub>2</sub> at between 200° and 300°.	Loses all its water of crystallisation below 260°, and at a bright red heat is completely decomposed, leaving ZnO.	Melts easily, and at a red heat sublimes unchanged.
Cadmium	Not affected.	Behaves like the preceding compound.	Loses CO <sub>2</sub> at a red heat, leaving the oxide CdO.	Loses all its water of crystallisation at a red heat.	Melts below a red heat, and sublimes at a higher temperature.

*Table showing the General Characteristics of the Compounds of the Principal Metals of the Zinc Group, their Chief Points of Resemblance and Dissimilarity, and their Distinctive Tests :—*

	OXIDE	SULPHIDE	GENERAL CHARACTERISTICS OF SALTS	DISTINCTIVE TESTS OF THE METAL IN SOLUTION
Magnesium	White and insoluble in water.		The magnesium salts are colourless and mostly soluble, the carbonate and ammonia-phosphate are insoluble.	No precipitate, with $H_2S$ or $NH_4S$ White precipitate, with $KHO$ , insoluble in excess. White crystalline, precipitate of $MgNH_4PO_4 + Aq$ , with $NH_3$ , and soda phosphate. No precipitate, with ammonium carbonate in the cold. White sulphide only formed in alkaline or neutral solutions by action of $H_2S$ .
Zinc	White and insoluble in water, turns yellow on heating — white again on cooling.	White and insoluble in water.	Carbonate and phosphate, white and insoluble, other ordinary salts soluble and colourless.	White precipitate with $KHO$ , and with $NH_3$ , soluble in excess of re-agent of $H_2S$ , on acid solutions.
Cadmium	Brown and insoluble in water.	Yellow and insoluble.	Resemble those of Zinc.	White precipitate $KHO$ , not soluble in excess. White precipitate with $NH_3$ , soluble in excess.

## THE IRON GROUP

## IRON

SYMBOL, Fe

COMBINING WEIGHT, 56

**DISTRIBUTION.**—Iron is a widely-diffused and very abundant element. Besides its almost universal presence in the mineral kingdom, it is found in small quantities in animals and vegetables, in the animal kingdom being a constituent of the red colouring matter of blood. Iron is occasionally met with in the free state principally in meteorites, but the whole of the metal of commerce is obtained from native compounds. The chief iron ores are *Hematite*,  $\text{Fe}_2\text{O}_3$ , occurring in the anhydrous and hydrated forms; *magnetic iron ore* or *loadstone*,  $\text{Fe}_3\text{O}_4$ ; *clay ironstone*, an impure ferrous carbonate, containing clay, silica, and calcium carbonate; and *black band ironstone*, also impure carbonate mixed with bituminous matter.

**PREPARATION.**—Pure iron may be prepared in the form of a powder, by reducing the heated oxide in a current of hydrogen, but the powder so produced takes fire on exposure to air, reforming the oxide. A button of the pure metal may be obtained by exposing a mixture of fine iron wire and oxide to a very high temperature in a covered crucible. Commercial iron is never pure, containing a greater or lesser amount of impurities, according to the kind of metal, its mode of preparation, and the description of ore from which it is obtained. Three varieties of metal are met with in commerce, viz., wrought-iron, which is the purest, steel which is less pure, and cast-iron which is the most impure. The smelting of iron ores is carried out on an immense scale in this country, the chief ores employed being Hematite and clay ironstone, the latter being principally used for the production of cast iron. Metallic iron used formerly to be prepared from the very rich

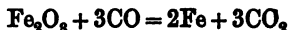


Hematites, which consist of a nearly pure oxide, by reducing them with charcoal, the spongy metallic masses obtained being hammered to cause coherence of the particles into a more solid form. This method has now been altogether superseded by the introduction of the blast furnace, by which any ore of iron may be reduced, and cast-iron obtained, which may subsequently, by suitable treatment, be refined and converted into wrought-iron or steel. The blast furnace generally employed is a tall structure of solid brick work and masonry, the interior of which is widest at about one-third of its height from the ground; from its widest diameter it tapers to the top, where it narrows to an opening of about ten feet in width, and also towards the bottom or hearth, the diameter of which is from three to nine feet. Near the top of the furnace are lateral openings closed by iron doors, and by which the charges of ore and fuel are introduced, and at the base or hearth are the blast pipes or "*tuyeres*" through which a blast of hot air is driven. The first step in the manufacture of the metal is the calcination of the ore, by which the water and carbonic acid are expelled, and ferric oxide left. The calcined ore is then mixed with a due proportion of broken limestone, and coal or coke, and the mixture is then placed in the furnace. The first change which takes place on the contact of the ore with the burning materials is the reduction of the ferric oxide to metallic iron by the heated carbonic oxide proceeding from the lower layers of burning fuel. As the mass sinks down in the furnace, it becomes more strongly heated, and the metal comes into intimate contact with the carbon of the fuel, with which it unites to form a fusible carbide of iron, while the impurities of the ore consisting of clay, silicious matter, etc, form fusible silicates or "*slag*" with the limestone. The melted materials finally reach the base or hearth of the furnace, where a partial reduction of silica takes place, the silicon formed uniting with the liquid iron.

The melted metal and slag collect in the hearth of the furnace, in two layers, the iron being beneath the slag. The furnace is periodically "tapped," the fused metal being run off into moulds, when it forms pig iron, the slag being drawn off by a separate channel. The changes which take place from the first treatment of the ore to the final production of metal may be divided into three stages :—

1. The conversion of ferrous carbonate into ferric oxide,  $2\text{FeCO}_3 + \text{O} = \text{Fe}_2\text{O}_3 + 2\text{CO}_2$ .

2. The reduction of the ferric oxide to metallic iron by the heated carbonic oxide,



3. The union of the metallic iron in the first place with carbon, and in the second with silicon, to form the fusible compound known as "cast-iron."

Ordinary pig-iron contains, besides carbon, some silicon and small quantities of phosphorus and sulphur. In this crude condition it is used for a great number of purposes, and is met with in commerce as white, grey, and mottled cast-iron, the grey variety being the most fusible, and therefore the most preferred for castings. Cast-iron is converted into wrought-iron, by a refining process, the chief feature of which is the elimination of its contained impurities. This is accomplished by a process called "puddling." The heated metal is exposed to a current of air in a reverberatory furnace. By this treatment the carbon, silicon, sulphur, and phosphorus are oxidised, the melted metal becoming coated with oxide, and losing its fusibility, so that it is eventually rolled into large balls. The balls are hammered to give the metal coherence; and finally passed between rollers to squeeze out the slag formed from the oxidation of silicon. The mass of metal is generally re-heated, and rolled a second time. This rolling process gives the iron a fibrous nature, which

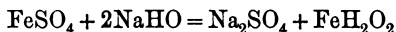
makes it capable of bearing great strains, but if subsequently submitted to long continued vibration or concussion, the metal loses its fibrous nature and becomes crystalline, its tensile strength being at the same time materially weakened. Wrought or malleable iron is the purest form in which the metal is met with in commerce, but it is never absolutely free from carbon and other impurities. Wrought-iron is converted into steel by placing bars of the metal in charcoal, and exposing them to a full red heat for several days. The metal takes up a certain amount of carbon, becomes more fusible and less malleable, and acquires all the properties of steel. This method of manufacture has been to a great extent superseded by the invention of the Bessemer process, whereby no less than six tons of pig iron can be converted into steel in twenty minutes. In this process cast-iron in a molten state is run into a large vessel working on trunions, called "*the converter*," and a blast of air at a pressure of about 20lb. to the square inch is then forced into the liquid metal, when the carbon is rapidly oxidised and eliminated, and the silicon converted into silica. When the whole of the carbon is thus removed, a charge of Spiegeleisen (an alloy of iron and manganese containing a large quantity of carbon) is introduced in sufficient quantity to furnish the requisite amount of carbon to convert the iron into steel, and the product is then run off into moulds.

**PROPERTIES.**—Pure iron has a bright white metallic lustre, crystallises in cubes, and is very ductile and tenacious. Its specific gravity is 7·8, and it requires a high temperature for its fusion. The metal may be softened by exposure to bright red heat, and separate pieces may then be welded together by hammering, and made to form a perfect joint. The physical properties of iron are not only considerably modified by the presence of comparatively small quantities of such elements as carbon, silicon, phosphorus, and sulphur, but also by the mechanical-manipulations to which the

metal is subjected. Thus hammered iron exhibits a granular and semi-crystalline fracture, while, if subjected to repeated rolling, it acquires a fibrous texture, and its tenacity is considerably increased. The properties of iron, more especially in the form of steel, are also greatly effected by *annealing* and *tempering*; thus, if heated to redness and slowly cooled, the metal is comparatively pliable, and may be bent, retaining the shape which it is made to take, whereas, if suddenly cooled by plunging whilst red-hot into water, it becomes hard and brittle. Iron is strongly attracted by the magnet, the magnetism induced being temporary in the case of pure soft iron, and more or less permanent in the case of steel. Iron is not affected by pure dry air, and even retains its lustre in perfectly pure water, but in ordinary air or water, in which carbonic acid is present, iron oxidises or *rusts*, hydrated ferric oxide being formed. Heated in the air, the metal becomes covered with black scales of the magnetic or black oxide, and the same oxide is formed when steam is passed over red hot iron. Iron is a tetrad, it forms two basic oxides,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , called ferrous and ferric oxides respectively. Each of these oxides forms a distinct class of salts, called ferrous and ferric, the colour of the former being green, and that of the latter yellow. The uses of iron are too well known to need description.

#### PRINCIPAL COMPOUNDS

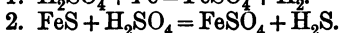
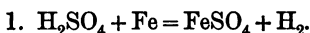
IRON MONOXIDE.—Ferrous oxide, Protoxide of Iron,  $\text{FeO}$ , is scarcely known in the absolutely pure condition owing to its tendency to absorb oxygen and pass into ferric oxide. In the hydrated form,  $\text{FeH}_2\text{O}_2$ , it is thrown down as a white precipitate by the addition of an alkali to a ferrous salt.



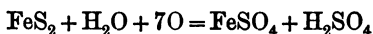
The precipitate rapidly changes colour on exposure to

air, becoming first green and then red from absorption of oxygen. The green colour of ordinary bottle glass is due to the presence of ferrous oxide.

**FERROUS SULPHATE**,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ , is a soluble salt prepared in large quantities for the manufacture of ink and the formation of black dyes. It may be produced by dissolving metallic iron or the sulphide in dilute sulphuric acid.



One equivalent of iron, viz., 56 parts, or one equivalent of  $\text{FeS} = 88$  parts when acted on by one equivalent of  $\text{H}_2\text{SO}_4 = 98$  parts, will yield one equivalent of  $\text{FeSO}_4 = 152$  parts, or 278 parts of the crystallised salt  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ . The quantities of the respective materials which must be taken to produce any given amount of ferrous sulphate thus admits of easy calculation. Ferrous sulphate is prepared on a large scale by the slow oxidation of iron pyrites,  $\text{FeS}_2$ . When the substance is exposed to the air in heaps, kept moist by watering, the following action occurs:—



From this equation it will be seen that in the oxidation of iron pyrites, although all the sulphur becomes oxidised to sulphuric acid, sufficient iron is present to unite with only half the acid formed. One-half only of the original sulphur in the pyrites can, therefore, be obtained by this natural oxidation process as  $\text{FeSO}_4$ . Suppose, for instance, that pyrites containing much earthy matter is submitted to oxidation for the purpose of procuring  $\text{FeSO}_4$ ; let it be assumed that it contains only 37·5 per cent of sulphur (pure  $\text{FeS}_2$  contains 53·3 per cent. of S), and that the amount of material taken amounts to 230 tons. Now, 230 tons at 37·5 per cent. of S gives a total of 86·25 tons of sulphur. As one-half only of the total sulphur pro-

duces  $\text{FeSO}_4$ , the available sulphur will be  $86.25 + 2 = 43.125$  tons. The equivalent of S being 32, and that of  $\text{FeSO}_4 + 7\text{H}_2\text{O}$  being 278, the amount of crystallised sulphate of iron equivalent to 43.125 tons of S is thus found :—

$$32 : 43.125 :: 278 : x$$

$$x = 374.64 \text{ tons of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$$

Ferrous sulphate forms large green crystals, which on exposure to air soon become covered with a reddish-yellow crust, from partial conversion into ferric sulphate. Ferrous sulphate is known in commerce as *copperas* and *green vitriol*.

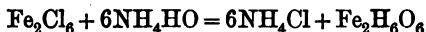
**FERROUS CHLORIDE**,  $\text{FeCl}_2$ , may be produced in the anhydrous form as a white sublimate by passing hydrochloric acid or chlorine gas over heated metallic iron. In solution, it is formed when the metal or its sulphide is treated with hydrochloric acid. It may be obtained from the solution in green crystals having the composition  $\text{FeCl}_2 + 4\text{H}_2\text{O}$ .

**FERROUS SULPHIDE**,  $\text{FeS}$ , is formed when iron is heated with sulphur, and as a black precipitate when sulphide of ammonium is added to a solution of a ferrous salt. Ferrous sulphide is largely used in the laboratory for the preparation of sulphuretted hydrogen. The disulphide,  $\text{FeS}_2$ , occurs native as iron pyrites.

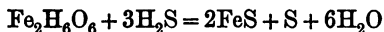
**FERROUS CARBONATE**,  $\text{FeCO}_3$ , occurs native as spathose iron ore, and as a constituent of clay ironstone. In the hydrated form, this substance, although insoluble in pure water, is dissolved to a small extent by water impregnated with carbonic acid; and it is in this form that iron is present in ferruginous waters. Hydrated ferrous carbonate is rapidly changed to ferric oxide by exposure to air.

**BLACK OR MAGNETIC IRON OXIDE**,  $\text{Fe}_3\text{O}_4$ , occurs native as loadstone or magnetic iron ore, and is formed when iron is heated in air or water vapour.

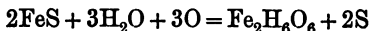
**FERRIC OXIDE** (sesquioxide of iron),  $\text{Fe}_2\text{O}_3$ , in the native condition, is a valuable ore of iron, occurring hydrated as bog ore, and anhydrous as hematite. Ferric oxide, in the hydrated form, is precipitated as a bulky gelatinous powder, of a reddish-brown colour, on the addition of an alkali to a solution of ferric salt—



In the anhydrous form, ferric oxide may be produced as a dark-red powder by heating ferrous sulphate to redness. Hydrated ferric oxide is easily soluble in acids, but the anhydrous oxide only dissolves with difficulty in the strongest acids by prolonged heating. Ferric oxide is used as a paint, and, in a finely-divided form, for polishing purposes, in which condition it is known as "Jewellers' Rouge." In the hydrated form, it is used for purifying coal-gas from sulphuretted hydrogen—



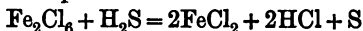
By exposing the material to the air, the ferrous sulphide is oxidised, sulphur being separated, and hydrated ferric oxide being formed—



The *revivified* material is then again ready for use, and is thus employed repeatedly for the same purpose.

**FERRIC CHLORIDE**,  $\text{Fe}_2\text{Cl}_6$  (perchloride of iron), is obtained in solution by dissolving ferric oxide in hydrochloric acid, or by treating a solution of ferrous sulphate with an oxidising agent. In the anhydrous form it is obtained in red crystals by passing an excess of chlorine over heated iron. These crystals are deliquescent, being very soluble in water, and also dissolved by alcohol. Ferric chloride in solution is converted into a ferrous salt by the action of reducing agents.

Sulphuretted hydrogen acts on it in this way with precipitation of sulphur—



FERRIC SULPHATE,  $\text{Fe}_2\text{3SO}_4$ , is obtained as a yellowish-white deliquescent mass by evaporating the solution obtained by dissolving ferric oxide in sulphuric acid.

### TESTS FOR IRON

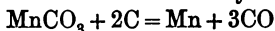
The reactions of iron in solution vary with the condition of the metal, whether a ferric or a ferrous salt is being examined. Ferric salts give a blood-red coloration with a solution of ammonium sulphocyanide, no change of colour appearing with a ferrous salt. Potassium ferrocyanide gives a light-blue precipitate with ferrous salts, and a dark-blue precipitate with ferric compounds. The ferrous compounds are green, and yield a white or greenish-white precipitate with caustic alkalis; the ferric compounds are yellow, and give a reddish-brown precipitate with caustic alkalis.

### MANGANESE

SYMBOL, Mn      COMBINING WEIGHT, 55

DISTRIBUTION.—Manganese is a moderately abundant element, being found in nature in combination with oxygen. The chief ore is the dioxide or pyrolusite,  $\text{MnO}_2$ , commonly called black oxide of manganese, the other native compounds being the sesquioxide,  $\text{Mn}_2\text{O}_3$ , or braunite, the hydrated sesquioxide,  $\text{Mn}_2\text{O}_4\text{H}_2$ , or manganite, and a further oxide, hausmanite,  $\text{Mn}_3\text{O}_4$ .

PREPARATION.—Metallic manganese is prepared by heating any of its oxides with charcoal to a very high temperature, or by treating a mixture of the carbonate with oil and charcoal in a similar way—



A fused button of metal is obtained, containing a little *carbon*.

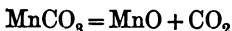


**PROPERTIES.**—The metal resembles cast-iron, being very hard and brittle, of a greyish-white colour, and only fusible at the highest temperature of the blast furnace; it has a specific gravity of 8·0, is rapidly oxidised in the air, decomposes water at ordinary temperatures. It is dissolved by hydrochloric and by dilute sulphuric acid, hydrogen being evolved in each case. Metallic manganese is not used in the arts, but an alloy of the metal with iron and carbon, called *spiegel-eisen*, is prepared on a large scale for use in the manufacture of Bessemer steel.

### PRINCIPAL COMPOUNDS

Manganese forms several classes of salts corresponding to the different oxides, the principal compounds being those of the protoxide, called manganous, and the sesquioxide, called manganic.

**MANGANESE MONOXIDE** (manganous oxide), **PROTOXIDE OF MANGANESE**,  $\text{MnO}$ , is produced as a greenish powder by heating the carbonate out of contact with air—



It rapidly absorbs oxygen from the air. In the hydrated form this oxide is thrown down as a white gelatinous precipitate by the addition of an alkali to a manganous salt. Manganous oxide forms with acids a well-defined series of salts of a pink colour.

**MANGANOUS SULPHATE**,  $\text{MnSO}_4 + 5\text{H}_2\text{O}$ , a crystalline soluble salt, of a pink colour, prepared by heating the dioxide with powdered coal, by which it is reduced to monoxide, and then dissolving the monoxide thus formed in sulphuric acid.

**MANGANESE CHLORIDE**,  $\text{MnCl}_2 + 4\text{H}_2\text{O}$  (protochloride of manganese), is obtained in pink tables by evaporating the solution remaining from the preparation of *chlorine* from manganese dioxide and hydrochloric acid.

It is deliquescent, and in the anhydrous state is soluble in alcohol.

**MANGANOUS CARBONATE**,  $\text{MnCO}_3$ , occurs native, and may be obtained in the hydrated form as a white precipitate by the action of alkaline carbonates on a manganous salt.

**MANGANESE SESQUIOXIDE** (manganic oxide),  $\text{Mn}_2\text{O}_3$ , is found native as braunite, may be prepared by heating manganous oxide to redness in contact with air,  $2\text{MnO} + \text{O} = \text{Mn}_2\text{O}_3$ ; but if the heat is too great, oxygen is given off, and manganoso-manganic oxide,  $\text{Mn}_3\text{O}_4$ , is formed. Manganic oxide forms a series of salts which are somewhat unstable; the most permanent compound being the so-called manganese alum, isomorphous with common alum, and in which  $\text{Mn}_2\text{O}_3$  replaces  $\text{Al}_2\text{O}_3$ .

**MANGANOSO-MANGANIC OXIDE**,  $\text{Mn}_3\text{O}_4$ , occurs native as hausmanite. It is the ultimate product of the action of a full red heat on any of the manganese oxides when fully exposed to the air.

**MANGANESE DIOXIDE**,  $\text{MnO}_2$ , is found native as pyrolusite; it may be prepared in the hydrated form by the addition of a solution of a hypochlorite to a manganous salt. By exposure to a continued red heat it is converted into manganoso-manganic oxide by loss of oxygen ( $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + 2\text{O}$ ).

Manganese dioxide is extensively used in commerce for the preparation of chlorine.

**MANGANIC ACID**.—When an oxide of manganese is heated with caustic potash with free exposure to air, a green mass is produced, which by treatment with cold water dissolves to a dark-green solution, from which crystalline potassium manganate,  $\text{K}_2\text{MnO}_4$ , may be obtained, isomorphous with the sulphate and chromate.

**PERMANGANIC ACID**,  $\text{HMnO}_4$ , is obtained by the action of sulphuric acid on barium permanganate. The potassium compound is prepared on a large scale by fusing

together manganese dioxide and potash with a little nitre, boiling the fused mass with water, and evaporating. Green potassium permanganate is first formed, the solution of which in boiling deposits hydrated manganese dioxide, and becomes purple from the formation of potassium permanganate. The salt crystallises in dark-purple red needles. Both manganates and permanganates readily part with oxygen, manganese dioxide being formed. It is this property which renders them such valuable disinfecting agents, their available oxygen rapidly oxidising putrescent organic matters. Solutions of potassium permanganate and manganate are sold for disinfecting purposes under the name of Condyl's Fluid. The solution of green potassium manganate is not only converted into the permanganate by heat, but by the action of acids, and the different shades of colour produced by the action of heat and alkalis have procured for it the name of "Mineral Chameleon."

MANGANESE SULPHIDE,  $MnS$ .—A flesh-coloured insoluble compound, precipitated on the addition of ammonium sulphide to a solution of a manganous salt.

#### TESTS FOR MANGANESE

The most characteristic test for the presence of manganese is the production of the green manganate by fusion with an alkali, the solution of which is coloured pink by the addition of an acid. The production of the flesh-coloured sulphide is also characteristic.

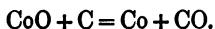
#### COBALT

SYMBOL,  $Co$                       COMBINING WEIGHT, 58.7

DISTRIBUTION.—Cobalt is found to a small extent *in the metallic state*, together with nickel and iron in *meteoric stones*, but its principal native ores are the

arsenide cobalt glance, and the sulphide, or cobalt pyrites.

**PREPARATION.**—The separation of cobalt from the various metals with which it is associated in the native ores, involves a series of chemical operations which could not be described, except at great length. The most difficult of all the associated metals to eliminate is nickel, which so far resembles cobalt in its re-actions as to render the process of separation exceedingly difficult. Metallic cobalt is generally prepared by first producing a pure oxide from the ore, and subsequently reducing the oxide at a high temperature with charcoal—



**PROPERTIES.**—Metallic cobalt is a hard infusible metal of a reddish white colour. It somewhat resembles iron in its infusibility, its tenacity, and in being strongly attracted by the magnet. Its specific gravity is 8.6. Cobalt does not tarnish in dry air, decomposes water at a red heat, and is soluble in hydrochloric, nitric, and sulphuric acids, hydrogen being evolved.

### PRINCIPAL COMPOUNDS

Cobalt forms two important oxides, the monoxide or cobaltous oxide, and the sesquioxide or cobaltic oxide. Several unimportant intermediate oxides are known. Cobalt forms two series of salts, the cobaltous and cobaltic, corresponding to the chief oxides.

*Cobaltous Oxide*,  $\text{CoO}$  (protoxide of cobalt, cobalt monoxide), is obtained in the hydrated form ( $\text{CoH}_2\text{O}_2$ ) as a pale rose-coloured precipitate by adding a solution of potassium hydrate to a cobaltous salt ( $\text{Co}_2\text{NO}_3 + 2\text{KHO} = 2\text{KNO}_3 + \text{CoH}_2\text{O}_2$ ). By igniting this hydrate the anhydrous oxide is obtained as a greenish grey or olive green powder ( $\text{CoH}_2\text{O}_2 = \text{CoO} + \text{H}_2\text{O}$ ). Cobaltous oxide dissolves in acids to form a series of rose-coloured

salts. An impure oxide, termed Zaffre, is used for colouring glass blue.

*Cobaltous Salts.*—Of these the chloride, sulphate, and nitrate are the most important; they are formed by dissolving the metal, monoxide, or carbonate, in the corresponding acids. The chloride is a very soluble salt, which is blue when anhydrous, but in the hydrated condition, forms red crystals,  $\text{CoCl}_2 + 6\text{H}_2\text{O}$ . The sulphate is a soluble salt, forming pink crystals,  $\text{CoSO}_4 + 7\text{H}_2\text{O}$ , and which is isomorphous with magnesium sulphate. The nitrate,  $\text{Co}_2\text{NO}_3 + 6\text{H}_2\text{O}$ , forms red crystals very soluble in water.

**COBALTIC OXIDE** (cobalt sesquioxide),  $\text{Co}_2\text{O}_3$ , is obtained when chlorine is passed through water containing the hydrated monoxide in suspension ( $2\text{CoH}_2\text{O}_2 + 2\text{Cl} = \text{Co}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{HCl}$ ). The precipitate must be heated cautiously to about  $600^\circ$  to render it anhydrous. Exposed to a higher temperature it loses oxygen, and is converted into an oxide,  $\text{CoO}, \text{Co}_2\text{O}_3$ . Cobaltic oxide when dissolved in acids forms cobaltic salts, which are, however, very unstable, and mostly known in solution only.

**COBALT SULPHIDE**,  $\text{CoS}$ , is a black compound insoluble in dilute acids, produced when a solution of any cobalt salt is treated with ammonium sulphide.

### TESTS FOR COBALT

The ordinary cobalt compounds form rose red solutions, which, when very concentrated, are blue. From the dilute solutions, potassium hydrate throws down the pink hydrated oxide. Ammonium sulphide precipitates the black sulphide. Before the oxidising flame of the blow-pipe, all cobalt compounds give, with fused borax, a characteristic blue bead.

## NICKEL

SYMBOL, Ni

COMBINING WEIGHT, 58.7

**DISTRIBUTION.**—Nickel occurs in nature principally as Kupfernickel, an arsenide Ni<sub>3</sub>As. It occurs in small quantities in the metallic state in meteorites, associated with cobalt and iron.

**PREPARATION.**—The metal is generally prepared from kupfernickel, and from speiss, an impure mixture of sulphide and arsenide, obtained in the extraction of cobalt from its arsenide. Like cobalt, nickel is obtained by a series of somewhat intricate chemical operations by which the arsenic and other associated metals are eliminated, and a comparatively pure nickel oxide is obtained, which is reduced at a high temperature with charcoal ( $\text{NiO} + \text{C} = \text{Ni} + \text{CO}$ ).

**PROPERTIES.**—Nickel is a silver white metal of specific gravity, 8.3. It is ductile and malleable, only fusible at a very high temperature, and possesses magnetic properties. The metal is soluble in hydrochloric, nitric, and sulphuric acids with evolution of hydrogen. Nickel is used extensively for the manufacture of nickel silver, an alloy of copper. The metal has also been used recently for electro-plating.

## PRINCIPAL COMPOUNDS

Nickel forms two oxides, the monoxide, or nickelous oxide, and the sesquioxide, or nickelic oxide. Only one class of salts is known, viz., those corresponding to the monoxide.

**NICKEL MONOXIDE** (nickelous oxide, protoxide of nickel), NiO, is produced as an apple-green hydrate, NiH<sub>2</sub>O<sub>2</sub>, on the addition of potassium hydrate to a nickelous salt. By the ignition of the hydrate, the anhydrous oxide is obtained as an olive-green powder, *soluble in acids, forming the ordinary nickel salts.*

**NICKELOUS SALTS.**—Of these the sulphate, nitrate and chloride, are the most important. They are produced by dissolving the metal, carbonate, or monoxide in the corresponding acids. They are all soluble in water. The sulphate forms green prisms,  $\text{NiSO}_4 + 7\text{H}_2\text{O}$ , the crystalline chloride has the composition  $\text{NiCl}_2 + 9\text{H}_2\text{O}$ , while the nitrate has a composition of  $\text{Ni}_2\text{NO}_3 + 6\text{H}_2\text{O}$ .

**NICKEL SESQUIOXIDE** (nickelic oxide),  $\text{Ni}_2\text{O}_3$ , is produced as a hydrate by passing chlorine gas through water, having nickelous oxide in suspension. It is a black powder which, by ignition, is converted into the monoxide with evolution of oxygen.

**NICKEL SULPHIDE**,  $\text{NiS}$ , a black insoluble compound, produced when ammonium sulphide is added to a solution of a nickel salt.

It has been already noticed that nickel forms only one class of salts, viz., those of the protoxide  $\text{NiO}$ . An acid solution of nickel is thus not changed by heating with an oxidising agent, such, for instance, as nitric acid, a treatment which converts a salt of the protoxide of iron into a salt of the sesquioxide.

#### TESTS FOR NICKEL

The salts of nickel have an apple-green colour, and their solutions, treated with potassium hydrate, give a pale green precipitate of the hydrated protoxide. Sulphide of ammonium gives a black sulphide insoluble in dilute nitric acid. In the oxidising flame of the blow-pipe, with borax, the nickel compounds give a reddish yellow bead, the colour of which fades on cooling.

#### SEPARATION OF NICKEL FROM COBALT

As these metals are generally associated in their *native ores*, and much resemble each other in their *compounds* and re-actions, their separation is often

attended with great difficulty. The two metals in solution may be more or less separated by several processes, of which two are here given as examples.

The first process to be described is founded on the fact that cobalt is precipitated from its neutral solutions by potassium nitrite in the form of a yellow compound (potassio-cobalt-nitrite), while nickel under similar conditions is not precipitated.

The acid solution of the mixed metals is concentrated to a small bulk, carefully neutralised with caustic potash, and solution of potassium nitrite added together with a little acetic acid. On standing for two days, the cobalt is precipitated as potassio-cobalt nitrite, while the nickel remains in solution. The precipitate is washed from adhering nickel with a solution of potassium chloride or sulphate, dissolved in hydrochloric acid, and the solution heated to expel nitrous acid, the cobalt being finally precipitated by the addition of potash. The solution of nickel may also be treated with potash, which separates the metal as hydrated oxide. The second method is founded on the fact that a current of chlorine, passed through an acid solution containing nickel and cobalt, causes the oxidation of the latter metal to sesquioxide, while the nickel suffers no change. By the subsequent addition of barium carbonate, the salt of cobalt sesquioxide is decomposed with precipitation of the oxide, the nickel salt being unaffected. In this process the acid solution of the two metals is largely diluted with water, and chlorine passed to excess, carbonate of barium to excess is then added, and the mixture shaken at intervals, and allowed to stand for about a day. The precipitate of cobalt sesquioxide, mixed with the excess of barium carbonate, is dissolved in hydrochloric acid, the barium precipitated as sulphate by the addition of dilute sulphuric acid, and the cobalt separated from the filtered solution by addition of potassium hydrate. *The solution of nickel, from which the cobalt has been*



separated, has the barium removed by dilute sulphuric acid, and the nickel precipitated by potassium hydrate.

#### GENERAL CHARACTERISTICS OF THE IRON GROUP

The metals of this group only decompose water at high temperatures. They all give insoluble hydrates, carbonates, and sulphides, and soluble sulphates and chlorides. The solutions all possess characteristic colours.

The following table shows the different characteristics of the compounds of the metals of the iron group, together with distinctive tests, and a further table shows the behaviour of the compounds under the action of heat.

[TABLE

	OXIDES	SULPHIDE	GENERAL CHARACTERISTICS OF SALTS	DISTINCTIVE TESTS FOR THE METALS IN SOLUTION
Iron	Insoluble $\text{FeO}$ , dark green $\text{Fe}_2\text{O}_3$ , red brown	Black insoluble	Ferrous salts are green, and ferric salts yellow. All ordinary compounds soluble except carbonate and phosphate.	Ferrous salts give a white pp with $\text{KFeCy}$ , and a green pp with $\text{KHO}$ . Ferric salts, a dark blue pp with $\text{KFeCy}$ , and a red pp with $\text{KHO}$ . Ferric salts also give a blood red coloration with a soluble sulphocyanate.
Manganese	Insoluble $\text{MnO}$ , greenish $\text{MnO}_2$ , black Chief oxides	Flesh coloured insoluble	Salts of manganese are pink, and (with the exception of carbonate and phosphate) soluble.	Pink sulphide only produced by $\text{H}_2\text{S}$ in neutral solutions; white pp with $\text{KHO}$ rapidly turning brown on exposure to air. Mn compounds give a green mass when fused with $\text{KNO}_3$ . Apple-green hydrate precipitated by $\text{KHO}$ . Carbonate of ammonia green pp soluble in excess. $\text{H}_2\text{S}$ precipitates black sulphide only from neutral or alkaline solutions.
Nickel	Insoluble $\text{NiO}$ Olive-green $\text{Ni}_2\text{O}_3$ , black	Black insoluble	Green and mostly soluble	Rose - coloured pp with $\text{KHO}$ of hydrate soluble in $\text{NH}_3$ , forming blue solution, $\text{H}_2\text{S}$ precipitates black sulphide only from neutral or alkaline solutions. Acetic acid and $\text{KNO}_3$ give yellow crystalline pp after some time. Co gives deep blue bead with borax in blow-pipe oxidising flame.
Cobalt	Insoluble $\text{CoO}$ , greenish grey $\text{Co}_2\text{O}_3$ , black	Black insoluble	Rose-red, and mostly soluble	

*Table showing the Action of Heat on the Leading Compounds of the Metals of the Iron Group :—*

	OXIDES	SULPHIDES	SULPHATE	NITRATE	CHLORIDE
Iron	At a red heat in contact with air FeO becomes $\text{Fe}_2\text{O}_3$ . $\text{Fe}_2\text{O}_3$ is also converted into $\text{Fe}_3\text{O}_4$	Is not affected by even a white heat in a closed vessel, but in air $\text{SO}_2$ is given off, and $\text{Fe}_2\text{O}_3$ remains	Ferrous sulphate evolves 6 equivalents of water at $114^\circ$ , at a red heat decomposes evolving $\text{SO}_3$ , and leaving a basic salt, which is also decomposed at a strong heat, leaving $\text{Fe}_2\text{O}_3$ .	.....	Anhydrous ferrous chloride melts at a red heat, and then decomposes, yielding chlorine and ferric chloride. Ferric chloride sublimes at $100^\circ$ , but when strongly heated in air yields $\text{Fe}_2\text{O}_3$ and Cl.
Manganese	The oxides of manganese at a red heat are all converted into the oxide $\text{Mn}_2\text{O}_4$	At a red heat in the air evolves $\text{SO}_2$ , $\text{M}_2\text{O}_4$ being left	Loses its water of crystallisation at a moderate temperature, and bears a red heat without decomposition.	.....	Anhydrous manganous chloride melts at a dull red heat, and in the presence of moist air evolves HCl, and leaves $\text{Mn}_2\text{O}_4$ .

Nickel	NiO is unchanged by exposure to a red heat. $\text{Ni}_2\text{O}_3$ becomes NiO.	Is decomposed by ignition in air, $\text{SO}_2$ being given off, and NiO left.	Loses its water of crystallisation, and is partly decomposed at a strong red heat.	Is decomposed at a red heat evolving nitrous vapours, and finally leaving NiO.	The anhydrous salt sublimes at an incipient red heat.
Cobalt	CoO at a red heat passes into a higher oxide. $\text{Co}_2\text{O}_3$ at a low red heat becomes $\text{CoO}$ , $\text{Co}_2\text{O}_3$ by loss of O.	By ignition in air $\text{SO}_2$ is formed, and $\text{CoO}$ , $\text{Co}_2\text{O}_3$ remains.	Loses its water of crystallisation, and becomes anhydrous at a red heat. Long continued exposure to a strong red heat partly decomposes the salt.	Melts below $100^\circ$ , loses water of crystallisation, and at a red heat evolves nitrous vapours, and leaves $\text{CoO}$ , $\text{Co}_2\text{O}_3$ .	At a red heat cobalt chloride partly sublimes, and is in part decomposed.

## THE TIN GROUP

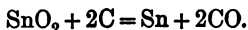
## TIN

SYMBOL, Sn

COMBINING WEIGHT, 118

DISTRIBUTION.—Tin is a moderately abundant element, but is not so widely distributed as many of the other metals. It does not occur in nature in the metallic state, but is met with as oxide,  $\text{SnO}_2$ , in cassiterite or tin stone, and as sulphide,  $\text{SnS}_2$ , in tin pyrites. The chief localities in which the ores are found are Cornwall, Malacca, and Saxony.

PREPARATION.—In the smelting of tin the ore, which generally contains a certain amount of the sulphides of copper and iron, is picked over and sorted, and then crushed to a comparatively fine powder by means of a stamping mill, the earthy particles being washed away by a stream of water. The washed ore is then calcined, by which the iron sulphide is decomposed, and the copper sulphide more or less oxidised. The calcined mass is then exposed to the air in heaps for a few days, by which the oxidation of the copper sulphide is completed, copper sulphate being formed, which is removed by lixiviation. The admixed ferric oxide is next eliminated by washing in a stream of water, and the purified tin ore is then smelted with powdered charcoal and a little lime, the lime forming a fusible slag with any earthy impurities present, while the carbon reduces the tin oxide to the metallic state—



The crude metal is finally purified by “liquation” and “boiling.” In the process of liquation the ingots of impure metal are subjected to a moderate heat, by which the comparatively pure metal fuses, and the foreign metals—such as iron and copper—are left

combined with part of the tin as a more infusible alloy. The purified tin is then remelted, and logs of wet wood plunged into the liquid metal, occasioning a sort of violent agitation resembling boiling, in which the remaining impurities rise to the surface, and are skimmed off. The purified metal is then cast into ingots.

**PROPERTIES.**—Tin is a bright white metal, of specific gravity 7.3; it is soft and very malleable, but possesses little tenacity. It emits a peculiar crackling noise when bent. It does not oxidise by exposure to air; melts at  $235^{\circ}$ ; and by exposure in the air to a higher temperature catches fire, forming the oxide  $\text{SnO}_2$ . The best solvent for tin is hydrochloric acid. Tin is largely employed in the arts for a variety of purposes. One of its most important uses is for coating such metals as iron and copper, in order to protect their surfaces from oxidation. The so-called tin plate consists of sheet-iron coated with tin. Tin-foil is largely employed when amalgamated with mercury for making mirrors. The alloys of the metal are numerous, but the most important are pewter, Britannia metal, solder, speculum metal, gun metal, and bell metal. The metallic tin of commerce generally contains small quantities of arsenic, lead, iron, and copper, as impurities.

### PRINCIPAL COMPOUNDS

Tin forms two oxides,  $\text{SnO}$  and  $\text{SnO}_2$ , and two classes of salts, termed stannous and stannic compounds respectively.

**TIN MONOXIDE.**—Stannous oxide,  $\text{SnO}$ .—When a stannous salt is precipitated with an alkaline carbonate, stannous hydrate,  $\text{SnH}_2\text{O}_2$ , is formed, which, when exposed to a heat not exceeding  $80^{\circ}$ , in an atmosphere of hydrogen or carbonic acid, loses water, and leaves the anhydrous oxide as a brown or black powder

( $\text{SnH}_2\text{O}_2 = \text{SnO} + \text{H}_2\text{O}$ ). Stannous oxide is insoluble in water, and very slightly attacked by acids in the cold; but when boiled, slowly dissolves with formation of a stannous salt.

**TIN DIOXIDE.**—Stannic oxide,  $\text{SnO}_2$ , is found native as cassiterite. It is formed when tin is strongly heated in the air as a white or yellowish powder, insoluble in water or acids, but which, when fused with a caustic alkali, forms a soluble stannate. Stannic oxide in the hydrated form is known in two conditions, which, although possessing the same percentage composition, manifest different properties. By acting on tin with strong nitric acid, diluted with a small quantity of water, a crystalline white powder termed metastannic acid is obtained, which has the formula  $\text{Sn}_5\text{O}_{10}5\text{H}_2\text{O}$ . This hydrate is insoluble in water and in strong acids; but hydrochloric acid forms with it a compound which, although insoluble in the acid, dissolves in pure water. Metastannic acid dissolves slowly in alkalis, forming metastannates.

The hydrate,  $\text{SnO}_2\text{H}_2\text{O}$ , called stannic acid, is precipitated by adding an acid to an alkaline stannate. It is easily dissolved by acids and alkalis, forming with the former stannic salts, and with the latter stannates. The sodium compound,  $\text{Na}_2\text{SnO}_3 + 4\text{H}_2\text{O}$ , is used as a mordant in calico printing, and is formed by fusing stannic oxide with sodium hydrate.

**TIN CHLORIDES.**—Of these the dichloride, or stannous chloride, also called protochloride of tin,  $\text{SnCl}_2$ , is obtained by dissolving metallic tin in hydrochloric acid,  $\text{Sn} + 2\text{HCl} = \text{SnCl}_2 + 2\text{H}$ ; it forms needle-shaped crystals having the composition  $\text{SnCl}_2 + 2\text{H}_2\text{O}$ . The anhydrous chloride is produced by heating mercuric chloride and tin together. Stannous chloride is a powerful reducing agent—reducing gold, silver, and mercury to the metallic state from many of their solutions. This action is due to the tendency of the stannous chloride to pass into a stannic salt. Tin tetra

chloride or stannic chloride,  $\text{SnCl}_4$ , may be prepared in the anhydrous state by passing chlorine gas over heated tin, or by distilling an intimate mixture of four parts of mercuric chloride and one part of metallic tin. It is a colourless fuming liquid, which boils at  $120^\circ$ , and unites, with a small quantity of water, with great evolution of heat, to form a soft mass, formerly known as "Butter of Tin;" from this a crystalline hydrate may be obtained,  $\text{SnCl}_4 + 5\text{H}_2\text{O}$ . Stannic chloride in solution is prepared for use as a mordant by dissolving metallic tin in nitro-muriatic acid (aqua regia).

The action of the tin salts in dyeing is due to the deposition of hydrated stannic oxide in the fibres of the material, the oxide having the power of absorbing and fixing many colouring matters.

**TIN SULPHIDES.**—Of the compounds of tin with sulphur, the most important is stannic sulphide,  $\text{SnS}_2$ , a bright yellow powder called mosaic gold, obtained by heating together tin, mercury, sulphur, and ammonium chloride, and also produced as a yellow precipitate by passing sulphuretted hydrogen through a solution of a stannic salt. Stannous sulphide,  $\text{SnS}$ , is produced as a dark grey mass by heating together sulphur and tin, and as a black precipitate on passing a current of sulphuretted hydrogen through a solution of a stannous salt.

#### TESTS FOR TIN

The reactions of tin in solution are dependent on whether a stannic or a stannous salt is under examination. A stannous salt gives, with a solution of gold trichloride, a beautiful precipitate known as "purple of Cassius;" the tin salt must be in excess, as otherwise a reduction of gold to the metallic state occurs. Stannic salts produce a white precipitate with an alkali soluble in excess, and also a precipitate with ammonia and alkaline carbonates not soluble in excess.



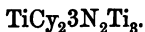
With sulphuretted hydrogen, a dirty yellow precipitate, soluble in caustic alkalies and their sulphides. All the tin salts can be easily reduced to the metallic state by exposure to the reducing flame of the blow-pipe on charcoal. A bright white metallic bead is obtained, which, when crushed between the teeth, emits a peculiar crackling noise.

## TITANIUM

SYMBOL, Ti

COMBINING WEIGHT, 50

TITANIUM is one of the rarer metals. It is found in the titaniferous iron sand of Cornwall, and also as rutile, which is an oxide. The metal is obtained as a dark-green heavy amorphous powder by heating the double fluoride of potassium and titanium with potassium. Titanium resembles tin in its compounds, forming titanous and titanic oxides,  $\text{TiO}$  and  $\text{TiO}_2$ , and two chlorides,  $\text{TiCl}_3$  and  $\text{TiCl}_4$ . Titanium is tetravalent, and is peculiar in directly uniting with nitrogen. Crystals are formed in the slags of blast furnaces of a bright copper colour, and were formerly supposed to be metallic titanium; it was, however, shown by Wöhler that the crystals are a compound of cyanide and nitride of titanium, represented by the formula



### GENERAL CHARACTERISTICS OF THE TIN GROUP

Tin and titanium do not decompose water except at high temperatures. They are both tetravalent. They form insoluble oxides and volatile tetrachlorides. The salts are colourless.

*The following Table shows the Action of Heat on the Principal Compounds of Tin:—*

OXIDES	SULPHIDES	CHLORIDES
At a red heat, in contact with air, $\text{SnO}$ becomes $\text{SnO}_2$ , $\text{SnO}_2$ at a red heat is chemically unchanged, but assumes a transient dark yellow or brown colour.	The sulphides of tin by prolonged heating in contact with air lose sulphur as $\text{SO}_2$ , while $\text{SnO}_2$ remains.	Stannous chloride melts at $250^\circ$ , and boils at a heat near redness. Stannic chloride boils at $115^\circ$ .

## THE CHROMIUM GROUP

### CHROMIUM

SYMBOL, Cr

COMBINING WEIGHT, 52.2

**DISTRIBUTION.**—Chromium is by no means an abundant metal, yet its compounds are comparatively numerous, and are extensively used in the arts for the production of pigments. The chief ore of chromium is chrome ironstone,  $\text{FeOCr}_2\text{O}_3$ , found in the Shetland Isles, in America, in Sweden, and in Australia. Chromium is also met with as lead chromate,  $\text{PbCrO}_4$ .

**PREPARATION.**—Metallic chromium is difficult to obtain, owing to the extremely high temperature which is necessary for its production. It is generally prepared by mixing the oxide with charcoal, and placing the mixture in a charcoal-lined crucible, which is subsequently exposed to a very high temperature. The oxide is then reduced by the carbon, metallic chromium and carbonic oxide being formed,  $\text{Cr}_2\text{O}_3 + 3\text{C} = 2\text{Cr} + 3\text{CO}$ .

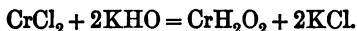
**PROPERTIES.**—Chromium appears to be the most infusible of all the metals. It burns when heated in the air, is violently attacked by nitric acid, and

is also dissolved by hydrochloric and sulphuric acids. Chromium has been obtained in the crystalline form.

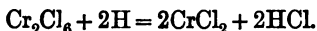
### PRINCIPAL COMPOUNDS

Chromium forms several oxides represented by the formulæ,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_3\text{O}_4$ , and  $\text{CrO}_3$ , and two classes of salts—these corresponding to the monoxide,  $\text{CrO}$ , being designated *chromous* compounds, and those corresponding to the sesquioxide,  $\text{Cr}_2\text{O}_3$ , termed *chromic* compounds.

CHROMIUM MONOXIDE, chromous oxide,  $\text{CrO}$ , has not yet been obtained in the anhydrous condition. In the hydrated form it is precipitated as a dark-brown powder by adding potash to a solution of chromous chloride—



CHROMIUM DICHLORIDE, chromous chloride,  $\text{CrCl}_2$ , is formed by passing a current of pure dry hydrogen over chromic chloride heated to redness. Hydrochloric acid and chromous chloride are formed—



It is a white crystalline body, dissolving in water with great evolution of heat, forming a blue solution, which rapidly absorbs oxygen from the air, and becomes green. It is one of the most powerful of the known reducing agents.

CHROMIUM SESQUIOXIDE, chromic oxide,  $\text{Cr}_2\text{O}_3$ .—When ammonia is added to a solution of a chromic salt, chromic hydrate,  $\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O} = \text{Cr}_2\text{H}_6\text{O}_6$ , is precipitated as a bulky gelatinous powder of a dark-green colour. By igniting this powder, water is expelled, and the anhydrous oxide obtained ( $\text{Cr}_2\text{H}_6\text{O}_6 = \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O}$ ). As thus obtained, chromic oxide is a dark-green infusible powder, insoluble in water and acids. It is largely used as a pigment, and in calico printing.

**CHROMIC CHLORIDE**,  $\text{Cr}_2\text{Cl}_6$ , is obtained in the anhydrous condition, in the form of violet crystals, by passing a current of chlorine over a mixture of chromic oxide and charcoal heated to redness ( $\text{Cr}_2\text{O}_3 + 3\text{C} + 6\text{Cl} = \text{Cr}_2\text{Cl}_6 + 3\text{CO}$ ). As thus prepared, it is insoluble in water, but will dissolve if the smallest quantity of chromous chloride is present. A solution of chromic chloride may be prepared by boiling a solution of chromic acid, or a chromate with hydrochloric acid and alcohol. The solution rapidly changes colour from yellow to bluish-green, the alcohol reducing the chromic acid to chromic oxide, and being itself reduced to aldehyde.

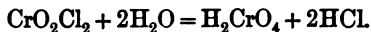
**CHROMIC SULPHATE**,  $\text{Cr}_2\text{3SO}_4$ , is formed in solution by boiling potassium dichromate with alcohol and sulphuric acid. It is remarkable for forming a double salt with potassium sulphate, known as chrome alum, of which the composition is  $\text{Cr}_2\text{K}_2\text{4SO}_4 + 24\text{H}_2\text{O}$ . It is isomorphous with common alum.

**CHROMIUM TRIOXIDE**,  $\text{CrO}_3$ , is obtained by mixing an excess of strong sulphuric acid with a strong solution of potassium dichromate. The chromium trioxide separates out from the cooled solution in needle-shaped crystals of a ruby-red colour. They are deliquescent, very soluble in water, with which they form chromic acid,  $\text{H}_2\text{CrO}_4$ , and when exposed to heat melt, ultimately decomposing into chromium sesquioxide and oxygen ( $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + 3\text{O}$ ). Chromic acid is a most powerful oxidising agent. The alkaline chromates are used in the arts for the manufacture of the chrome colours. Potassium dichromate is the chief of these salts, known in commerce as bichromate of potash. This is prepared direct from chrome iron ores. The ore is finely powdered, and mixed with potassium carbonate and a little potassium nitrate, and the mixture fused. The iron of the ore is converted into insoluble sesquioxide, while the chromium is converted into the trioxide, which unites with the potassium to form potassium

chromate,  $K_2CrO_4$ , a yellow salt, isomorphous with the sulphate. By adding to a strong solution of the chromate sufficient sulphuric acid to combine with half the base, potassium dichromate,  $K_2Cr_2O_7$ , is formed ( $2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O$ ). The salt crystallises in orange-red four-sided tables. The chromates of many of the metals are insoluble, and of characteristic colour. Lead chromate,  $PbCrO_4$ , is bright yellow, and is the well-known chrome yellow. Silver chromate,  $Ag_2CrO_4$ , and mercury chromate,  $HgCrO_4$ , are both deep red and insoluble, while barium chromate is pale yellow.

The chromates of the heavy metals, and dichromates of the alkalis, are decomposed by exposure to a red heat, chromium sesquioxide being formed, and oxygen given off.

CHLORO-CHROMIC ACID, chromyl chloride,  $CrO_2Cl_2$ , is a deep-red, fuming liquid, formed by distilling an intimate mixture of sodium chloride and potassium dichromate with sulphuric acid. Chloro-chromic acid is decomposed by water with formation of chromic and hydrochloric acid—



It is a powerful oxidising agent, and, when dropped on a piece of sulphur or phosphorus, sets fire to it.

#### TESTS FOR CHROMIUM.

Chromium is generally met with in the chromic condition. The chromic salts are generally green, and yield a dirty-green precipitate with ammonia. This precipitate, if fused with a little potassium nitrate, gives a yellow mass of alkaline chromate. All the non-volatile chromium compounds are converted into alkaline chromate by fusion with a mixture of potassium carbonate and nitrate, and the solution gives a yellow precipitate with a lead salt, red precipitate with a silver

compound, and is turned green by boiling with hydrochloric acid and alcohol. Borax fused with chromium sesquioxide assumes a fine deep green colour. The following table shows the action of heat on the more important chromium compounds :—

*The Action of Heat on the more Important  
Compounds of Chromium :—*

OXIDES	CHLORIDES	POTASSIUM DICHROMATE
The hydrated protoxide, $\text{CrH}_2\text{O}_2$ , is converted by ignition into $\text{Cr}_2\text{O}_3$ . $\text{Cr}_2\text{O}_3$ is unaltered at all ordinary temperatures, but melts at the heat of a forge fire.	Chromous chloride, $\text{CrCl}_2$ , and chromic chloride, $\text{Cr}_2\text{Cl}_6$ , when heated to redness in air, evolve chlorine, and leave $\text{Cr}_2\text{O}_3$ .	Melts below a low red heat to a transparent liquid. At a white heat, oxygen is evolved, and a mixture of neutral chromate and chromium sesquioxide is left.

## MOLYBDENUM

SYMBOL, Mo

COMBINING WEIGHT, 96

THIS element may be classed among the rarer metals. It is met with in nature as molybdenite, which is a sulphide, and as lead molybdate, or wulfenite. It is a white, brittle metal, and forms three oxides,  $\text{MoO}$ ,  $\text{MoO}_2$ , and  $\text{MoO}_3$ . The last oxide is a yellow powder, and unites with water to form molybdic acid. A nitric acid solution of molybdic acid is used in the laboratory as a test for small quantities of phosphoric acid, with which it forms an insoluble compound. Molybdenum forms two classes of salts, termed respectively molybdous and molybdic. They are comparatively unimportant, and have no special applications.

## TUNGSTEN, OR WOLFRAM

SYMBOL, W                      COMBINING WEIGHT, 184

DISTRIBUTION.—Tungsten is a metal which is found in nature as wolfram, a tungstate of iron and manganese, a somewhat abundant mineral, and as scheelite, a tungstate of calcium.

PREPARATION.—The metal may be obtained by passing the vapour of tungstic chloride over strongly-heated sodium.

PROPERTIES.—As thus obtained, the metal forms a steel-grey powder, which can only be aggregated into globules by a very intense heat.

## PRINCIPAL COMPOUNDS

Tungsten forms two oxides,  $\text{WO}_2$  and  $\text{WO}_3$ , and two chlorides,  $\text{WCl}_4$  and  $\text{WCl}_6$ . The trioxide, tungstic oxide,  $\text{WO}_3$ , is obtained by heating the native calcium compound with nitric acid; it unites with bases to form a series of salts. Tungstous oxide,  $\text{WO}_2$ , is produced when the trioxide is heated in an atmosphere of hydrogen. The tungsten salts are numerous, but the majority of them are comparatively unimportant. The most important salt is the sodium compound,  $\text{Na}_2\text{WO}_4$ , which is colourless and soluble, and is used for rendering fabrics unflammable. The addition of small quantities of tungsten to steel imparts to it a great degree of hardness, and endows it with other valuable properties.

## URANIUM

SYMBOL, U                      COMBINING WEIGHT, 240

URANIUM is a somewhat rare metal, found as pitchblende,  $\text{U}_3\text{O}_8$ , as uranite, which is a phosphate, and in some other minerals. The metal is prepared by acting

on the protochloride with sodium; it resembles iron in colour, tarnishes on exposure to air, and has a specific gravity of 18.4. It does not decompose water at ordinary temperatures, but dissolves in acids with evolution of hydrogen, forming a well-defined series of salts. Uranium forms four oxides, only two of which are important, viz., uranous oxide,  $\text{UO}_2$ , and uranic oxide,  $\text{UO}_3$ , and two corresponding classes of salts, the uranous and the uranic. Of these, the former are green and the latter yellow. Uranic oxide forms, with bases, a series of compounds termed uranates, which are mostly insoluble in water. The sodium compound is used as a pigment, under the name of "Uranium yellow," chiefly for staining glass and porcelain. Uranous oxide imparts a fine black colour to glass. The chief salts of uranium are the nitrate and acetate.

#### CHARACTERISTICS OF THE GROUP

The metals of this group only decompose water at a high temperature. They all form trioxides, which are more or less acid compounds, forming salts with bases. The lower oxides are insoluble.



*Table showing the Characteristics of the Principal Compounds of the more Important Metals of the Chromium Group, together with their Distinctive Tests:—*

	SULPHIDE	OXIDES	CHLORIDES	DISTINCTIVE TESTS
Chromium	Not formed in aqueous solution.	<p><math>\text{CrO}</math>, only known as a brown hydrate, <math>\text{CrH}_2\text{O}_2</math>;  <math>\text{Cr}_2\text{O}_3</math> is a dark-green infusible powder.  <math>\text{CrO}_3</math> is a ruby-red crystalline substance, very soluble in water, and forming important salts termed chromates.</p>	<p><math>\text{CrCl}_3</math> (chromous chloride) is a white crystalline substance, soluble in water, with which it forms a blue solution.  <math>\text{Cr}_2\text{Cl}_6</math> (chromic chloride) is in the anhydrous form a crystalline substance, of a violet colour, not readily soluble in pure water, but freely dissolving in the presence of <math>\text{CrCl}_3</math>.</p>	An insoluble chromium compound, when fused with a mixture of carbonate and nitrate of an alkali, yields a yellow mass, soluble in water, which gives a yellow precipitate with solution of lead acetate, and a red one with solution of silver nitrate. Boiled with $\text{HCl}$ and alcohol, the solution changes colour to a deep bluish-green.

Tungsten	Black and insoluble.	as an acid to bases, forming uranates, which are for the most part insoluble.	uranic, soluble in water. Uranic oxychloride, $\text{UO}_2\text{Cl}_2$ , is yellow, crystalline, and soluble in water.	salts are yellow. A uranic salt gives a deep red-brown precipitate, with potassium ferrocyanide, which dissolves in excess of $\text{NH}_3$ to a colourless solution.
		$\text{WO}_3$ (tungstous oxide) is a brown insoluble powder. $\text{WO}_3$ is insoluble and yellow, uniting with bases to form tungstates. The sodium compound is soluble.	Tungsten forms several chlorides, the chief of which are the dichloride, $\text{WCl}_2$ , and the hexachloride, $\text{WCl}_6$ . $\text{WCl}_6$ forms dark violet scales. $\text{WCl}_5$ is dark-grey and amorphous.	Solutions of tungsten are colourless. If a solution of tungsten is acidified with $\text{HCl}$ , and a bar of zinc placed in the solution, a blue colour is produced.

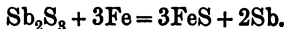
## THE ANTIMONY GROUP

## ANTIMONY

SYMBOL, Sb.      COMBINING WEIGHT, 122

DISTRIBUTION.—Antimony is found native in the metallic state, but its chief ore is the trisulphide,  $\text{Sb}_2\text{S}_3$ , known as *Stibnite*.

PREPARATION.—Metallic antimony is generally extracted from the native sulphide by fusing it with scrap iron, the iron uniting with the sulphur to form ferrous sulphide, while the antimony is set free—

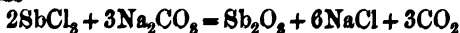


Before being subjected to this treatment the ore is fused, in order to free it from adhering earthy matters. The metal may also be obtained by roasting the ore, when sulphurous oxide passes off, and a mixture of oxide and sulphide is left, and then finally reducing the mixture by fusion with charcoal and sodium carbonate. The crude metal is generally purified by fusion with American potash.

PROPERTIES.—Antimony is a very brittle metal, of a bluish-white colour, and fine metallic lustre. It fuses at  $430^\circ$ , and volatilises at a white heat. Its specific gravity is 6.7. Antimony is not changed in the air at ordinary temperature, but in the melted condition it becomes quickly oxidised, and at a still higher temperature burns with a white flame, producing the trioxide,  $\text{Sb}_2\text{O}_3$ . When acted on by strong hydrochloric acid metallic antimony is converted into the trichloride, with evolution of hydrogen. Dilute hydrochloric and sulphuric acids have no action on it, while strong nitric acid violently attacks it with formation of the pentoxide,  $\text{Sb}_2\text{O}_5$ . Antimony is used in the arts for the manufacture of type metal, for which it is alloyed with lead, and also for Britannia metal.

## PRINCIPAL COMPOUNDS

ANTIMONY TRIOXIDE, antimonious oxide,  $\text{Sb}_2\text{O}_3$ , is the product of the oxidation of antimony when heated in the air. It is, however, more conveniently obtained by the action of an alkaline carbonate on the trichloride—



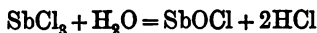
Antimony trioxide is a white powder which forms a series of salts with the stronger acids. In the hydrated state it is often called Antimonious acid, and is capable of playing the part of a weak acid, uniting with the alkalies to form *antimonites*, but these compounds are somewhat unstable. The most important salt produced from antimonious oxide is that formed by dissolving it in a solution of acid potassium tartrate. The solution on concentration yields crystals of the double tartrate of antimony and potassium, or *tartar emetic*,  $\text{C}_4\text{H}_4\text{KSbO}_7 + \text{Aq}$ .

ANTIMONY TETROXIDE,  $\text{Sb}_2\text{O}_4$ , is a white infusible powder produced by heating metallic antimony in the air until no further increase of weight takes place. This compound is sometimes regarded as a mixture of the trioxide and the pentoxide.

ANTIMONY PENTOXIDE.—Antimonic oxide,  $\text{Sb}_2\text{O}_5$ , is produced in the hydrated condition by the action of strong nitric acid on metallic antimony. In this state it is termed antimonic acid ( $\text{HSbO}_3$ ), but by exposure to a moderate heat it is converted into the anhydrous oxide. As thus produced it is a yellowish powder, insoluble in water and acids, and which, when heated to redness, gives off oxygen, and is converted into the tetroxide. Antimony pentoxide when fused with sodium or potassium hydrate forms an antimoniate, from which antimonic acid can be separated. A distinct hydrate called metantimonic acid ( $\text{H}_4\text{Sb}_2\text{O}_7$ ) is precipitated by the action of water on the pentachloride.

The acid sodium metantimonate,  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ , is remarkable for being the only insoluble salt of sodium.

**ANTIMONY TRICHLORIDE**,  $\text{SbCl}_3$ , is obtained in solution by dissolving metallic antimony or its sulphide in strong hydrochloric acid,  $\text{Sb}_2\text{S}_3 + 6\text{HCl} = 3\text{H}_2\text{S} + 2\text{SbCl}_3$ . The salt itself may be procured by subjecting the solution to distillation, when the trichloride volatilises and solidifies to a mass of crystals. Antimony trichloride is also formed when the powdered metal is shaken into chlorine gas, in which it takes fire spontaneously. It is also formed by passing a current of chlorine over an excess of the metal in a tube when the trichloride is produced as a soft mass, sometimes called *butter of antimony*. Antimony trichloride is decomposed by water on insoluble oxychloride,  $\text{SbOCl}$  being produced—



**ANTIMONY PENTACHLORIDE.**—Antimonic chloride  $\text{SbCl}_5$  is a colourless volatile liquid produced by the action of an excess of chlorine on metallic antimony, or by passing chlorine over the trichloride. It is decomposed by heat into antimony trichloride and free chlorine, and when acted upon by a limited quantity of water produces the oxychloride,  $\text{SbOCl}_3$ , but with an excess of water it forms metantimonic acid.

**ANTIMONY SULPHIDES.**—Antimony forms two sulphides,  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$ , corresponding to the two oxides. The compound  $\text{Sb}_2\text{S}_3$  is the native ore, and black in colour; while the artificially prepared substance produced by the action of sulphuretted hydrogen on an acid solution of the trichloride, is of a bright orange tint. This sulphide is an ingredient of the so-called Bengal lights. The compound,  $\text{Sb}_2\text{S}_5$ , is comparatively unimportant.

**ANTIMONIURETTED HYDROGEN**,  $\text{SbH}_3$ , is formed by the action of nascent hydrogen on any of the soluble

antimony compounds. It is an inflammable gas, burning with a bluish flame, and evolving a white smoke of antimony trioxide. When a cold body is depressed into the flame, a deposit of metallic antimony takes place, and, when passed into silver nitrate solution, a black precipitate of antimonious argentide  $\text{SbAg}_3$  is produced. The distinction between these reactions and those produced under similar circumstances from arseniuretted hydrogen, will be noticed under arsenic.

#### TESTS FOR ANTIMONY

The most characteristic reactions of antimony are the production of the orange sulphide on the addition of  $\text{H}_2\text{S}$  to the acid solution, the decomposition and precipitation of the chlorides by water, and the formation of the gaseous hydrogen compound.

### ARSENIC

SYMBOL, As

COMBINING WEIGHT, 75

DISTRIBUTION.—Arsenic is occasionally met with in the free state, but more frequently in combination with metals as arsenides, principally with iron, cobalt, nickel, and copper. It is also found associated with sulphur.

PREPARATION.—Arsenic in the metallic state is prepared either by distilling the native arsenide of iron, or arsenical pyrites, in earthenware retorts, or by reducing arsenious acid by heating it with charcoal.

PROPERTIES.—Arsenic is very brittle, and is of a steel-grey colour. Its specific gravity is 5.6 to 5.9. It crystallises in rhombohedra, and at a dull red heat volatilises without previous fusion, the vapour having a peculiar odour of garlic. Heated in the air, it takes fire and burns with a bluish flame, forming the trioxide,  $\text{As}_2\text{O}_3$ . Arsenic is peculiar in resembling a metal in its physical properties, but in being more allied to phosphorus and nitrogen in its chemical characters.

The atom of arsenic weighing 75 occupies, when in the gaseous state, a volume only half as large as that of the atoms of the majority of the other elements in the same condition. The *vapour density* of arsenic is therefore twice 75, or 150.

### PRINCIPAL COMPOUNDS

**ARSENIC TRIOXIDE**, arsenious anhydride,  $\text{As}_2\text{O}_3$ . This oxide is formed when metallic arsenic is burnt in the air, or when any of the arsenical ores are roasted with free exposure to air. It is produced in very large quantity by roasting arsenical pyrites,  $\text{FeSAs}$ , and is the arsenious acid, or *white arsenic* of commerce. As generally met with, it is a heavy white powder, of specific gravity 3.6, volatilising at  $220^\circ$  without previous fusion. Arsenic trioxide occurs in two distinct forms, viz., the vitreous, in which it is a semi-transparent glass-like solid; and the crystalline, in which it occurs in brilliant octahedra. Arsenic trioxide is only soluble in water to a small extent; the solution has a feebly acid reaction, and contains arsenious acid,  $\text{H}_3\text{AsO}_3$ . Arsenic trioxide is more soluble in water containing hydrochloric acid than in pure water, and is freely dissolved by alkalies, forming salts called arsenites, having the general formula  $\text{M}_3\text{AsO}_3$ . The arsenites of the alkalies are soluble in water, while those of the alkaline earths and of the heavier metals are insoluble. The copper compound constitutes the well-known pigment called *Scheele's green*. Arsenic trioxide, as well as the arsenites, and arsenic compounds generally, are powerful poisons.

**ARSENIC PENTOXIDE**.—Arsenic anhydride,  $\text{As}_2\text{O}_5$ , is generally called arsenic acid, although this term more properly applies to the product of the reaction of the oxide on water, having the formula  $\text{H}_3\text{AsO}_4$ . Arsenic pentoxide is prepared by the action of nitric acid on the trioxide, the solution obtained being evaporated

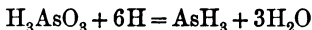
to dryness to expel the excess of nitric acid. It is a white, noncrystalline powder, soluble in water, the solution yielding crystals of  $\text{H}_3\text{AsO}_4$  on evaporation. When strongly heated arsenic pentoxide evolves oxygen and becomes  $\text{As}_2\text{O}_3$ . Arsenic acid forms salts called arseniates.

**SULPHIDES OF ARSENIC.**—Arsenic unites with sulphur to form three compounds—the disulphide,  $\text{As}_2\text{S}_2$ , found in nature as Realgar; the trisulphide,  $\text{As}_2\text{S}_3$ , also found native as Orpiment; and the Pentasulphide,  $\text{As}_2\text{S}_5$ . The sulphide prepared by passing sulphuretted hydrogen through a solution of arsenious acid is the trisulphide or orpiment, and precipitates as a bright yellow powder.

The sulphides of arsenic unite with the sulphides of the alkali metals to form soluble compounds known as sulpharsenites and sulpharsenates; thus, neutral sulpharsenite of potassium has the formula  $2\text{K}_2\text{S}.\text{As}_2\text{S}_3$ , while the neutral sulpharsenate is  $2\text{K}_2\text{S}.\text{As}_2\text{S}_5$ .

Arsenic also unites with chlorine, bromine, and iodine. The most important of these compounds is the trichloride,  $\text{AsCl}_3$ , which is a colourless volatile liquid, boiling at  $132^\circ$ , and decomposed by water with formation of arsenious and hydrochloric acids.

**ARSENIC and HYDROGEN, ARSENIURETTED HYDROGEN,**  $\text{AsH}_3$ , is produced whenever nascent hydrogen acts on any of the arsenic compounds. It may be prepared by placing arsenic trioxide into a hydrogen apparatus together with zinc, and dilute sulphuric acid. The hydrogen evolved by the action of the zinc on the sulphuric acid acts at the moment of its liberation on the arsenious acid, thus—



Arseniuretted hydrogen may also be obtained by the action of dilute sulphuric acid on an alloy of zinc and arsenic. It is a colourless gas, having an odour resembling that of garlic, and burning in the air with



a blue flame, forming arsenic trioxide and water. If the supply of air is limited, the hydrogen alone burns, and metallic arsenic is liberated; the gas is also decomposed into metallic arsenic and free hydrogen by passage through a red-hot tube.

#### ANALOGY BETWEEN THE COMPOUNDS OF ARSENIC AND THOSE OF PHOSPHORUS AND NITROGEN

The general chemical analogy of these three elements will be seen by comparing the formulæ of some of their leading compounds, thus—

	Oxides		Chlorides	Hydrides
Arsenic	$\text{As}_2\text{O}_3$	$\text{As}_2\text{O}_5$	$\text{AsCl}_3$	$\text{AsH}_3$
Phosphorus	$\text{P}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{PCl}_3$	$\text{PH}_3$
Nitrogen	$\text{N}_2\text{O}_3$	$\text{N}_2\text{O}_5$	$\text{NCl}_3$	$\text{NH}_3$

Arsenic and phosphorus also form corresponding acids, the arsenious,  $\text{H}_3\text{AsO}_3$ , and the phosphorous,  $\text{H}_3\text{PO}_3$ , the arsenic,  $\text{H}_3\text{AsO}_4$ , and the phosphoric,  $\text{H}_3\text{PO}_4$ . The arseniates resemble the corresponding tribasic phosphates—

Arsenic acid or trihydrogen

arsenate . . . . .	$\text{H}_3\text{AsO}_4$
Dihydrogen sodium arsenate . . . . .	$\text{H}_2\text{NaAsO}_4 + \text{H}_2\text{O}$
Hydrogen di-sodium arsenate . . . . .	$\text{HNa}_2\text{AsO}_4 + 12\text{H}_2\text{O}$
Tri-sodium arsenate . . . . .	$\text{Na}_3\text{AsO}_4 + 12\text{H}_2\text{O}$

The salt,  $\text{HNa}_2\text{AsO}_4 + 12\text{H}_2\text{O}$ , cannot be distinguished from ordinary phosphate of soda in appearance; and its solution, mixed with ammonium chloride, ammonia, and magnesium sulphate, gives a white crystalline precipitate of  $\text{NH}_4\text{MgAsO}_4 + 6\text{H}_2\text{O}$ , corresponding to the similar phosphorus compound.

#### TESTS FOR ARSENIC

The detection of arsenic in medico-legal inquiries is often of the greatest importance, and its separation and

identification is fortunately comparatively simple. All compounds of arsenic, without exception, are capable of forming, in contact with nascent hydrogen, arseniuretted hydrogen, and on this circumstance is founded "*Marsh's Test.*" Into a small apparatus for generating hydrogen (Fig. 8) is placed some pure zinc and some dilute sulphuric acid. The outlet tube of the apparatus is drawn out to a fine jet, and the hydrogen evolved is lit as it issues from this jet, and burns with a small blue flame. A piece of white porcelain is now depressed into the flame for a few seconds, when, in the event of the zinc and acid being free from arsenic, no discoloration of the white porcelain will take place. Having thus established the purity of the re-agents used, the substance



Fig. 8

to be tested for arsenic is introduced into the hydrogen apparatus, the jet of gas relighted and again tested by the depression of the cold porcelain. If there is still no discoloration of the white surface arsenic is absent; if, however, the least trace of arsenic is present, a dark brilliant metallic spot will appear on the porcelain. This result can only accrue from the presence of arsenic or antimony, and the two deposits may be distinguished by the fact of the solubility of that of arsenic in a solution of sodium hypochlorite. If the evolved gas be passed into a solution of silver nitrate, the presence of arsenic will cause a black deposit of metallic silver, while the liquid will contain the arsenic as arsenious acid. By heating a portion of the outlet tube with a flame, any arsenic present is deposited as a black metallic ring. The successful application of Marsh's test to organic liquids frequently requires the previous destruction of organic matter to prevent the liquid from frothing when placed in the hydrogen apparatus.

**REINSCH'S TEST.**—A little dilute hydrochloric acid is boiled with a few slips of bright copper foil; if the

lustre of the metal remains unaffected, the materials are free from arsenic. The suspected liquid is then introduced and heat again applied for a few minutes, when, if arsenic is present, it will be deposited on the copper as a grey film. The slips of copper are then removed, washed, dried, and introduced into a glass tube, to which heat is applied, when the arsenic is converted into arsenious oxide, which sublimes and forms a ring of minute octahedral crystals. Finally, arsenious acid in solution gives—with solution of silver nitrate and dilute ammonia, a yellow precipitate of silver arsenite, soluble in excess of ammonia and nitric acid; acidified with hydrochloric acid, and treated with sulphuretted hydrogen, a yellow precipitate of the trisulphide; with copper sulphate and dilute alkali, a precipitate of Scheele's green. Arsenic acid gives a reddish brown precipitate with a solution of silver nitrate.

## BISMUTH

SYMBOL, Bi

COMBINING WEIGHT, 210

**DISTRIBUTION.**—Bismuth is a comparatively rare metal, and is found in nature, principally in the metallic state, chiefly in Saxony. It is also met with in the form of sulphide.

**PREPARATION.**—The metal is obtained by the simple process of exposing its ores to the action of heat in sloping cylinders of cast-iron, when the bismuth melts, and drains away from the earthy impurities with which it is associated.

**PROPERTIES.**—Bismuth is a brittle metal of a peculiar reddish-white colour and crystalline appearance. Its specific gravity is 9·8, it melts at 265°, and at a high temperature may be volatilised. When a mass of the metal is melted and allowed to cool slowly, it crystallises in large rhombohedra. Bismuth does not oxidise in

the air at ordinary temperatures, but when strongly heated it burns with a blue flame forming the oxide. The best solvent for the metal is nitric acid. In the arts bismuth is used chiefly for the preparation of fusible alloys, one of which melts below  $100^{\circ}$ . The compounds of bismuth much resemble those of antimony. Some of them are used in medicine.

### PRINCIPAL COMPOUNDS

**BISMUTH TRIOXIDE, BISMUTHOUS OXIDE,  $\text{Bi}_2\text{O}_3$ ,** is a pale yellow powder, formed when the metal is heated in the air, or when the nitrate is decomposed by heat. It fuses by exposure to a high temperature.

**BISMUTH PENTOXIDE, BISMUTHIC OXIDE,  $\text{Bi}_2\text{O}_5$ ,** is a powder of a reddish-brown colour, formed by dissolving the trioxide in potash, and precipitating by nitric acid with the aid of heat. Bismuth pentoxide is converted into the trioxide by exposure to heat, and, like the corresponding antimony compound, forms soluble salts with the alkalies.

**BISMUTH NITRATE,  $\text{Bi}_3\text{NO}_3 + 5\text{H}_2\text{O}$ ,** is formed by dissolving the metal in nitric acid. It is the most important of the bismuth salts, and is occasionally used in medicine. Its solution is decomposed by the addition of a large quantity of water, an insoluble subnitrate being deposited as a white powder, which is used in commerce as a pigment under the name of flake white.

**BISMUTH TRICHLORIDE,  $\text{BiCl}_3$ ,** is formed when the metal is thrown into chlorine gas, the union being attended with the evolution of light and heat. It is decomposed by water, an insoluble oxychloride,  $\text{BiOCl}$ , being deposited. The pearl white of commerce is an oxychloride of bismuth. Bismuth sulphide,  $\text{Bi}_2\text{S}_3$ , is thrown down by sulphuretted hydrogen from solutions containing the metal as a black powder.

## TESTS FOR BISMUTH

The most characteristic reactions of the bismuth compound are the production of the black sulphide by the action of sulphuretted hydrogen on the acid solutions, the decomposition of the salts by dilution with a large bulk of water, and the ease with which a bead of brittle metal may be obtained on charcoal in the reducing flame of the blow-pipe.

## VANADIUM

SYMBOL, V

COMBINING WEIGHT, 51.3

Vanadium is an exceedingly rare metal, found in certain iron and lead ores, and as Lead Vanadate. It forms several oxides, a tetrachloride, and two sulphides. The compounds of vanadium are allied in their properties to those of arsenic, antimony, and bismuth.

## GENERAL CHARACTERISTICS OF THE GROUP

The metals of this group are linked on the one hand by their physical properties to true metallic substances, and on the other hand by their chemical characteristics to the non-metallic elements, phosphorus and nitrogen. Two metals of the group, viz., arsenic and antimony, are peculiar in forming gaseous compounds with hydrogen. The chlorides of arsenic, antimony, and bismuth are all decomposed by water, and the pentoxides form salts with bases.

*Antimony Group, together with their Distinctive Tests:—*

	SULPHIDE	OXIDES	PRINCIPAL COMPOUNDS	DISTINCTIVE TESTS
Antimony	$Sb_2S_3$ bright orange and insoluble	Antimony forms two oxides, viz., $Sb_2O_3$ and $Sb_2O_5$ , a third and unimportant, $Sb_2O_4$ , is also known. $Sb_2O_3$ is a white powder insoluble in water, but soluble in solution of acid potassium tartrate, and in HCl. $Sb_2O_5$ is a light straw-coloured powder.	Antimony trichloride, $SbCl_3$ , a white solid. Antimony pentachloride, $SbCl_5$ , mobile, strongly fuming liquid. Antimoniretted hydrogen $SbH_3$ , gaseous and inflammable, decomposed by passage through a red-hot tube.	Solutions of antimony are characterised by being partially decomposed by dilution with an excess of water. Their acid solutions give an orange-coloured sulphide with $H_2S$ , and when treated with zinc and sulphuric acid yield antimoniretted hydrogen, which when burned evolves white fumes, and gives a black stain on a piece of cold porcelain.
Arsenic	$As_2S_3$ bright yellow and insoluble	Arsenic forms two oxides, the arsenious, $As_2O_3$ , and the arsenic $As_2O_5$ . $As_2O_3$ is the white arsenic of commerce, and is generally met with as a heavy white powder, very slightly soluble in	$AsCl_3$ is a heavy pungent fuming liquid, boiling at $132^\circ$ , and decomposed by water, with formation of $As_2O_3$ and HCl. $AsH_3$ (arseniretted hydrogen) is gaseous and inflammable.	Solutions of As are chiefly characterised by formation of a bright yellow sulphide, with $H_2S$ , precipitated in the presence of free acid, and by the formation of gaseous $AsH_3$ , when treated with zinc and dilute sulphuric acid. The evolved gas when burned

Table—Continued

	SULPHIDE	OXIDES	PRINCIPAL COMPOUND	DISTINCTIVE TESTS
Bismuth	$\text{Bi}_2\text{S}_3$ black and insoluble	water. $\text{As}_2\text{O}_5$ is crystalline and soluble in water.  $\text{Bi}_2\text{O}_3$ is a pale yellow insoluble powder. $\text{Bi}_2\text{O}_5$ is a reddish brown powder. $\text{Bi}_2\text{O}_5$ like the corresponding compounds of Sb and As, forms compounds with alkaline bases.	The Nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , is crystalline and soluble, but decomposed by a large addition of water. The chloride, $\text{BiCl}_3$ , is a deliquescent fusible solid, decomposed by water, with formation of an insoluble oxychloride, $\text{BiOCl}$ .	evolves white fumes of $\text{As}_2\text{O}_3$ and gives a black stain on a piece of cold porcelain. Neutral solutions containing $\text{As}_2\text{O}_3$ give with solution of $\text{CuSO}_4$ a green precipitate. Solutions of Bi give a black sulphide in the presence of free acid when treated with $\text{H}_2\text{S}$ . They are decomposed by dilution with a large quantity of water, a white insoluble basic salt generally precipitating, which is not dissolved by tartaric acid. This last reaction distinguishes bismuth from antimony, the basic salts of which are soluble in tartaric acid.

Table showing the Action of Heat on the Principal Compounds of the Leading Metals of the Antimony Group:—

	OXIDES	SULPHIDE	CHLORIDE	NITRATE
Antimony	$\text{Sb}_2\text{O}_3$ turns yellow when heated, melts below a red heat, and sublimes at a higher temperature, being partly converted into $\text{Sb}_2\text{O}_5$ in the presence of air. $\text{Sb}_2\text{O}_5$ at a red heat loses O and becomes $\text{Sb}_2\text{O}_4$ .	$\text{Sb}_2\text{S}_3$ melts at a low red heat, and may be volatilised at a white heat; in the presence of air $\text{SO}_2$ and $\text{Sb}_2\text{O}_3$ are formed.	$\text{SbCl}_3$ melts at $72^\circ$ , and boils at about $200^\circ$ . $\text{SbCl}_5$ is volatile at a comparatively low temperature.	
Arsenic	$\text{As}_2\text{O}_3$ volatilises at about $218^\circ$ . $\text{As}_2\text{O}_5$ is unaltered at a dull red heat, but is decomposed into $\text{As}_2\text{O}_3$ and $\text{O}_2$ by exposure to a full red heat.	$\text{As}_2\text{S}_3$ burns in the air when heated, forming $\text{SO}_2$ and $\text{As}_2\text{O}_3$ . When air is excluded, it may be volatilised at a red heat.	$\text{AsCl}_3$ boils at $132^\circ$ .	
Bismuth	$\text{Bi}_2\text{O}_3$ melts at a red heat. $\text{Bi}_2\text{O}_5$ loses a portion of its O at a temperature of a little over $100^\circ$ , and becomes $\text{Bi}_2\text{O}_4$ .		Melts and volatilises at a moderate temperature.	The crystallised salt melts in its water of crystallisation when exposed to a gentle heat. It is decomposed at a low red heat, $\text{Bi}_2\text{O}_3$ being left.



## THE LEAD GROUP

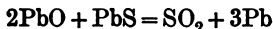
## LEAD

SYMBOL, Pb

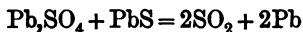
COMBINING WEIGHT, 207

**DISTRIBUTION.**—Lead is not found in nature in the free state, but occurs principally as sulphide or galena, PbS. It also occurs in smaller quantities as the carbonate or white lead ore,  $\text{PbCO}_3$ . The chief source of the metal is England and Spain.

**PREPARATION.**—The ore is picked, crushed, and washed by a stream of water, by which it is to a great extent freed from earthy matter. The ore is then roasted in a reverberatory furnace until part of the sulphide has passed by oxidation to sulphate, and a further portion has been converted into oxide by the conversion of its sulphur into sulphurous oxide. The temperature is then raised, when the oxide and unaltered sulphide react on each other with formation of sulphurous oxide and metallic lead, thus—



A further quantity of the unaltered sulphide is acted on by the lead sulphate, sulphurous oxide and metal being formed as before—



The lead thus obtained generally contains small quantities of antimony, copper, iron, and sometimes silver, which harden the metal to such an extent as to materially interfere with many of its most useful applications. The separation of silver from lead will be described under "Silver." The purification of lead is effected by a process called softening, in which the lead is melted, and exposed in a melted condition to *the action* of a current of air, when a scum is formed, *consisting* of lead oxide, together with the oxides of

other metals. This is skimmed off, and the lead is in a state of absolute purity.

PROPERTIES.—Lead is a metal having a peculiar bluish white colour, and a specific gravity of 11·3. It is so soft that it may be readily scratched by the nail, and leaves a metallic-looking streak on paper. It may be rolled into sheets, or drawn into wire; but it possesses but little tenacity. Lead does not tarnish in pure, dry air, but when exposed to a moist atmosphere becomes coated with oxide, the oxidation taking place more rapidly in the presence of carbonic acid. The action of water on lead has been already described. Lead melts at 335°, and at a high temperature is slightly volatile. Sulphuric and hydrochloric acids have but little action on lead, but the metal is freely dissolved by nitric acid. Lead is used in the arts for the manufacture of piping, for alloys, and in the form of sheet for lining water cisterns, forming sulphuric acid chambers, etc. With the addition of a little arsenic, lead is used for making shot, while its chief alloys are solder, type metal, pewter, and Britannia metal. The compounds of lead are all more or less poisonous.

### PRINCIPAL COMPOUNDS

Lead forms five oxides, but only one class of salts, many of which are, however, of great importance.

LEAD SUBOXIDE,  $\text{Pb}_2\text{O}$ , is formed when lead oxalate is heated to a temperature not exceeding 300°, with exclusion of air. It is a black powder.

LEAD MONOXIDE,  $\text{PbO}$  (protoxide of lead), is formed as a straw-coloured powder by heating the metal in a current of air. It is prepared on a large scale in commerce, and is known as massicot and litharge, used for the manufacture of lead glass. Lead monoxide is produced in the hydrated form by adding a caustic alkali to a solution of lead salt. Protoxide of lead *fuses at a red heat*, is soluble in solutions of caustic

alkalies, and unites with acids to form a series of salts. Lead oxide is readily reduced to metallic lead by heating in a current of hydrogen, water being formed. The combining weight of lead may by this means be ascertained. Supposing, for instance, that 100 grams of  $\text{PbO}$  when reduced by hydrogen lose 7.1724 grams, this loss of weight being entirely due to the separation of oxygen, the percentage composition of the lead oxide will be—

$$\left. \begin{array}{l} \text{O} = 7.1748 \\ \text{Pb} = 92.8252 \end{array} \right\} 100$$

The combining weight of oxygen being 16, we can then calculate the quantity of metallic lead needed for union with the equivalent of oxygen, and the quantity so found will be the equivalent of lead, thus—

$$7.1748 : 16 :: 92.8252 : x \\ x = 207$$

**LEAD DIOXIDE**, binoxide of lead,  $\text{PbO}_2$ , also called brown or puce oxide, is obtained by exposing the monoxide suspended in water to the action of a stream of chlorine gas, or by treating red lead with nitric acid. It is a brown powder, which, by exposure to a red heat, passes into the monoxide by loss of oxygen ( $\text{PbO}_2 = \text{PbO} + \text{O}$ ). When treated with sulphuric acid it also loses oxygen, and passes into the sulphate; while acted on by hydrochloric acid, lead chloride is formed, and chlorine evolved ( $\text{PbO}_2 + 4\text{HCl} = \text{PbCl}_2 + 2\text{H}_2\text{O} + 2\text{Cl}$ ).

**RED OXIDE OF LEAD (RED LEAD)** is a compound of the monoxide and dioxide, having the composition  $2\text{PbO} + \text{PbO}_2 = \text{Pb}_3\text{O}_4$ . It is prepared on a large scale by exposing litharge to a dull red heat, with free exposure to air, and is used in glass-making, and as a paint. Treated with dilute nitric acid, the lead monoxide is dissolved, and the dioxide left. A further lead oxide,  $\text{Pb}_2\text{O}_3$ , is also known.

**LEAD NITRATE**,  $\text{Pb2NO}_3$ , is a soluble, crystalline salt obtained by dissolving metallic lead, the carbonate, or the mon-oxide, in nitric acid. It is decomposed by exposure to a red heat ( $\text{Pb2NO}_3 = \text{PbO} + \text{N}_2\text{O}_4 + \text{O}$ ).

**LEAD CHLORIDE**,  $\text{PbCl}_2$ , is produced as a white precipitate on adding hydrochloric acid or an alkaline chloride to a moderately strong solution of lead nitrate. It

is soluble in about 33 parts of boiling water, the salt crystallising as the solution cools in six-sided shining needles. If a solution of lead chloride is treated with a solution prepared by dissolving metallic silver in nitric acid, the silver unites with the chlorine of the lead chloride to form insoluble silver chloride,  $\text{AgCl}$ ; and from the amount of silver necessary for the complete precipitation of a weighed quantity of the lead compound, the combining weight of lead may be calculated. As this reaction affords a good illustration of the method of determining the combining weight of an element, we will give the following example—if 4.9975 grams of  $\text{PbCl}_2$  require 3.881 grams of metallic silver for complete precipitation, what is the combining weight of lead, that of silver and chlorine being known? Now, as the combining weight of silver is 108, and that of chlorine is 35.5, the quantity of the latter element equivalent to 3.881 grams of silver is thus found—

$$\begin{array}{rclcl} 108 & : & 3.881 & :: & 35.5 & : & x \\ & & & & & & x = 1.2756 \end{array}$$

The 4.9975 grams of  $\text{PbCl}_2$  contain therefore 1.2756 grams of Cl, and 3.7219 of Pb ( $4.9975 - 1.2756$ ).

As 1.2756 grams of Cl are thus united to 3.7219 of Pb, the amount of Pb required for the two equivalents of chlorine in  $\text{PbCl}_2$  can be calculated, thus—

$$\begin{array}{rclcl} 1.2756 & : & 71 & (35.5 \times 2) & :: & 3.7219 & : & x \\ & & & & & & & x = 207 \end{array}$$

**LEAD SULPHATE**,  $\text{PbSO}_4$ , an insoluble salt formed as a heavy, white precipitate on adding sulphuric acid, or a soluble sulphate to a solution of a lead salt. It is found native in small quantities.

**LEAD ACETATE** is one of the most important lead compounds. It is prepared on a large scale by dissolving litharge in acetic acid. It crystallises in prisms, which are soluble in about half their weight of water. The salt has a sweet taste, and is hence familiarly known as sugar of lead. It is poisonous.

**LEAD CARBONATE**,  $\text{PbCO}_3$ , occurs native as cerusite, and is produced artificially as a white, insoluble precipitate on adding a cold solution of an alkaline carbonate to a solution of a lead salt. The white lead of commerce used so extensively as a paint, is a mixture of carbonate with hydrated oxide, having a composition more or less approximating to the formula  $2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$ . It is prepared in large quantities by a process called the Dutch method. In this process a number of small jars are partly filled with weak acetic acid (vinegar), and placed on spent tan or stable manure. In each jar is suspended a thin roll of sheet lead, and the whole series of jars is then covered with boards upon which is placed a further layer of manure or spent tan, which receives another series of jars, and the arrangement is continued until many successive alternations of boards, tan, and jars are thus built up. After a time the metallic lead is completely converted into a mixture of hydrated oxide and carbonate. The action appears to consist in the formation of basic acetate by the action of the acetic acid vapour upon the metallic lead, which is then converted into carbonate by the carbonic acid evolved by the fermenting tan or manure, the liberated acetic acid then acting on a fresh portion of the lead, which is also decomposed by a further quantity of carbonic acid, the two actions thus continuing until the change is complete.

**LEAD SULPHIDE**,  $\text{PbS}$ , occurs native as galena. It is

produced as a black precipitate by the action of sulphuretted hydrogen on a solution of lead.

Of the remaining lead salts, the most important are the iodide,  $PbI_2$ , which is produced as a yellow precipitate on mixing solutions of lead acetate and potassium iodide. The salt is soluble in boiling water, crystallising from the solution in brilliant golden scales. The chromate,  $PbCrO_4$ , a yellow insoluble compound, used as a pigment under the name of chrome yellow.

### TESTS FOR LEAD

The most characteristic reactions of lead are as follow: the production of the yellow chromate when a soluble lead salt is mixed with solution of potassium chromate; the formation of the yellow iodide; the black sulphide, when a stream of sulphuretted hydrogen is passed into a solution of a salt of the metal; and an insoluble white sulphate on the addition of sulphuric acid, or a solution of a sulphate. Before the reducing flame of the blow-pipe, mixed with sodium carbonate on a piece of charcoal, the compounds of lead readily yield a bead of the metal, which gives a dark streak when rubbed on white paper.

### THALLIUM

SYMBOL, Tl

COMBINING WEIGHT, 204

This metal was discovered by Crookes, in 1861, by the aid of spectrum analysis in the seleniferous deposit of a pyrites burner, and is one of the many additions that gentleman has made to chemical science.

DISTRIBUTION.—Thallium occurs in small quantities as sulphide in certain specimens of iron and copper pyrites as well as in some zinc ores.

PREPARATION.—The metal is obtained most economi-

cally from the dust which collects in the flues of the burners in which thalliferous pyrites is burnt for the production of sulphuric acid. This deposit contains from  $\frac{1}{4}$  to 3 per cent. of thallium, and is treated with hot water, the impure thallium chloride being precipitated from the solution by the addition of hydrochloric acid. This is converted into sulphate by heating the chloride with sulphuric acid, and the product is then purified. The metal is obtained by reducing the sulphate by means of pure zinc, and fusing the spongy metallic masses so obtained.

PROPERTIES. — Metallic thallium is of a brilliant white colour, free from any blue tint. It quickly tarnishes in the air. Its specific gravity is 11.8 and it melts at  $294^{\circ}$ , boils at a white heat, and may be distilled in an atmosphere of hydrogen. It dissolves easily in nitric and sulphuric acids.

#### PRINCIPAL COMPOUNDS

Thallium forms two oxides,  $Tl_2O$  and  $Tl_2O_3$ , and a corresponding series of salts, the thallious and the thallic salts.

THALLIUM OXIDES. — The monoxide or thallious oxide,  $Tl_2O$ , is formed from the gradual oxidation of the metal in moist air. It is soluble in water forming a hydrate  $TlHO$ ; the solution is alkaline, absorbs carbonic acid from the air, and forms by neutralisation with acids a well defined series of salts, isomorphous with the corresponding potassium compounds. The trioxide, or thallic oxide,  $Tl_2O_3$ , is a dark brown powder insoluble in water and alkalis, but soluble in acids, with which it forms a series of somewhat unstable salts. This oxide is formed when Thallium is heated in the air.

THALLIUM SALTS. — Of these the most important are thallious sulphate,  $Tl_2SO_4$ , and thallious chloride,  $TlCl$ . Thallic sulphate is a soluble salt crystallising in anhydrous, rhombic prisms. It forms a double salt

with aluminium sulphate,  $\text{Al}_2\text{Tl}_24\text{SO}_4 + 24\text{H}_2\text{O}$ , is amorphous with common alum.

**THALLIOUS CHLORIDE**,  $\text{TlCl}$ , is formed when the metal is brought into contact with a limited quantity of chlorine. It is very slightly soluble in water.

**THALLIOUS CARBONATE**,  $\text{Tl}_2\text{CO}_3$ , is a crystalline salt soluble in about twenty five parts of cold water.

**THALLIUM SULPHIDE**,  $\text{Tl}_2\text{S}$ , is black and insoluble.

### TESTS FOR THALLIUM

The thallium compounds are colourless ; they are also poisonous. The most characteristic distinctions of the metal in solution being the non-production of any precipitate with alkalis, or alkaline carbonates, or with sulphuric acid, and the formation of a comparatively insoluble chloride. Thallium compounds give a very characteristic spectrum consisting of a single brilliant green line.

### GENERAL CHARACTERISTICS OF THE GROUP

Lead and thallium are distinguished from all the preceding metals by the comparatively insoluble nature of their chlorides. The following tables show the chief characteristics of the compounds of the metals of the lead group, and the action of heat on the chief compounds.

[TABLE



*Table showing the Leading Characteristics of the Principal Compounds of the Metals of the Lead Group, together with their Distinctive Tests :—*

	OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDE	DISTINCTIVE TESTS
Lead	<p>PbO is a straw coloured powder insoluble in water, but dissolving in solutions of caustic alkalis.</p> <p>PbO<sub>2</sub> is a brown insbl. powder.</p> <p>Pb<sub>3</sub>O<sub>4</sub> is a heavy, red, and insoluble powder.</p> <p>It is generally regarded as a mixture of PbO and PbO<sub>2</sub>.</p>	PbS black and insoluble	PbSO <sub>4</sub> is a white heavy powder insoluble in water.	Pb(NO <sub>3</sub> ) <sub>2</sub> is a white crystalline salt freely soluble in water.	PbCl <sub>2</sub> is white and crystalline. It is not very soluble in water, one part of the salt requiring about 33 parts of boiling water.	Solutions of lead are colourless. They give a white soluble sulphate a white precipitate of PbSO <sub>4</sub> , with soluble chlorides (if the Pb solution is strong) a white precipitate of PbCl <sub>2</sub> . With solution of potassium chromate solutions of lead salts give a yellow precipitate of lead chromate, and with potassium iodide a light yellow precipitate of lead iodide, soluble in boiling water.
Thallium	<p>Tl<sub>2</sub>O is soluble in water, with which it forms a definite hydrate TlHO.</p> <p>Tl<sub>2</sub>O<sub>3</sub> is a dark brown powder which is insoluble in water.</p>	TlS black and insoluble	Tl <sub>2</sub> SO <sub>4</sub> is a soluble salt crystallising in colourless rhombic prisms which are anhydrous.	Unimpor- tant.	TlCl is a white compound which is very slightly soluble in water.	Thallium is chiefly distinguished by the solubility of its monoxide and sulphate, and the comparative insolubility of its chloride.

*Metals of the Lead Group:—*

	OXIDES	SULPHIDE	NITRATE	CHLORIDE	SULPHATE
Lead	PbO melts at a red heat to a clear dark red liquid. If kept at a <i>low</i> red heat for a considerable time it takes up O, and becomes Pb <sub>3</sub> O <sub>4</sub> . Pb <sub>3</sub> O <sub>4</sub> is resolved at a strong red heat into PbO and O. PbO <sub>2</sub> is first converted by heat into Pb <sub>3</sub> O <sub>4</sub> , and at a higher temperature into PbO. Tl <sub>2</sub> O melts to a brown limpid liquid below a red heat. Tl <sub>2</sub> O <sub>3</sub> at a red heat loses O and becomes Tl <sub>2</sub> O.	PbS melts at a strong red heat, and may be sublimed without change in the absence of air. If air is present, SO <sub>2</sub> is evolved and a mixture of metallic lead and sulphate of lead remains.	Pb <sub>2</sub> NO <sub>3</sub> is decomposed at an incipient red heat. $\text{Pb}_2\text{NO}_3 = \text{PbO} + 2\text{NO}_2 + \text{O}$	PbCl <sub>2</sub> heated to redness with exclusion of air simply fuses without change, but in the presence of air it emits white fumes, turns yellow, and is converted into an oxychloride.	Melts at a red heat without decomposition.
Thallium				TlCl melts below a red heat to a thin brown liquid.	

## THE SILVER GROUP

## SILVER

SYMBOL, Ag

COMBINING WEIGHT, 108

DISTRIBUTION.—Silver is met with in nature in the metallic state, but is chiefly found as ores, the principal of which are the sulphide or Silver Glance,  $\text{Ag}_2\text{S}$ , and the chloride or horn silver,  $\text{AgCl}$ . As sulphide, silver occurs mixed with lead sulphide, forming the argentiferous galena, from which a large quantity of the silver of commerce is obtained.

PREPARATION.—The method of extraction of metallic silver from the ore differs with the description of ore to be treated. The native sulphide is treated by roasting with common salt, the sulphide being converted into chloride during the process. The mixture is then agitated with water and scrap iron when the iron is converted into chloride, and the silver separated in the metallic state. Mercury is then added, which forms a liquid amalgam with the silver, and by subsequently distilling this amalgam, the silver is left. In the case of argentiferous galena, the lead is first prepared from the ore in the usual way, and the metal so obtained is afterwards subjected to Pattinson's process, by which the silver is separated, and the quality of the lead improved. This process is founded on the fact that an alloy of lead and silver will remain fluid at a considerably lower temperature than pure lead. The lead is melted in a cast-iron pot, and the temperature then lowered by the withdrawal of the fire. The metal at the same time is well stirred. Comparatively pure lead then crystallizes out, and is removed by a perforated ladle, while the fluid alloy of lead and silver remains behind. The whole of the silver originally present is thus obtained with a smaller admixture of lead. By repeating the process an alloy

is eventually obtained, containing about 300 ounces of silver to the ton, whereas the original lead did not contain perhaps more than three or four ounces. This rich silver alloy is then subjected to a process called "cupellation." It is melted in a reverberatory furnace on a porous bed made of bone ash, and a blast of air forced on the surface of the melted metal, by which the lead is gradually oxidised, the oxide formed then fuses, and is absorbed into the pores of the cupel until at length the silver is obtained with very little admixture with lead. By re-cupellation the silver is obtained pure. During the solidification of the melted silver, a curious phenomenon, known as "spitting," occurs. The melted metal has the singular property of absorbing about twenty-two times its own volume of oxygen, which is suddenly evolved at the moment of solidification, and gives rise to the phenomenon just mentioned.

**PROPERTIES.**—Silver is a metal of specific gravity 10·5, having a brilliant white colour. It does not tarnish in pure air, the discoloration observed to take place on silver articles being generally due to traces of sulphuretted hydrogen. The discoloration of silver in the pocket is due to the sulphur compounds in the sweat. Silver is malleable and ductile, and one of the best conductors of heat and electricity. The metal is extensively used for the manufacture of various articles for domestic and ornamental purposes, and also for electro-plating. "Standard" silver used for coinage, etc., contains 7·5 per cent. of copper, the alloy being harder than pure silver, and therefore better able to resist the wear and tear of daily use. Silver is easily dissolved by nitric acid.

#### PRINCIPAL COMPOUNDS

Silver forms three oxides,  $\text{Ag}_4\text{O}$ ,  $\text{Ag}_2\text{O}$ , and  $\text{Ag}_2\text{O}_2$ . Of these three the compound  $\text{Ag}_2\text{O}$  is the most impor-

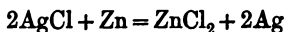
tant. Silver yields a series of well defined salts with acids.

**SILVER OXIDES.**—The suboxide,  $\text{Ag}_4\text{O}$ , is formed by passing hydrogen over silver oxalate heated to  $100^\circ$ ; it is a black powder which is readily decomposed. The monoxide,  $\text{Ag}_2\text{O}$ , is a brown powder, precipitated when potassium hydrate is added to a solution of silver nitrate. It is a strong base, from which any of the ordinary silver salts may be prepared by the action of acids. It is decomposed by a heat into oxygen and metallic silver. Silver dioxide,  $\text{Ag}_2\text{O}_2$ , is formed by the action of ozone on the finely divided metal. It is a black powder.

**SILVER NITRATE**,  $\text{AgNO}_3$ , is formed when metallic silver or the monoxide is dissolved in nitric acid. It is the most important salt of silver. It forms large tabular crystals soluble in an equal weight of cold water. The crystals fuse on heating. When these are fused and cast into sticks, it is known as lunar caustic, and is used in medicine as a cautery. Silver nitrate, when exposed to light in contact with organic matter, blackens, probably from formation of the suboxide. The salt is much used in photography and for making indelible marking ink.

**SILVER CHLORIDE**,  $\text{AgCl}$ , is met with in nature as horn silver, and is produced as a white curdy precipitate on the addition of hydrochloric acid or a soluble chloride to a solution of a silver salt. It is insoluble in nitric acid, but freely soluble in ammonia, in solution of sodium hyposulphite, and also to a small extent in hydrochloric acid and soluble chlorides. Silver chloride fuses at about  $260^\circ$ , and forms, when cool, a semi-transparent mass resembling horn. By exposure to a high temperature it volatilises. When exposed to the action of light, silver chloride becomes of a purple colour, due to a partial decomposition in which a subchloride is formed *and* hydrochloric acid set free. This change takes *place* with much greater rapidity in the presence of

organic matter, and it is this decomposition as well as that which occurs to the iodide and bromide under similar conditions that the operations of the photographic are based. The pictures produced are fixed by treating them with a solution of sodium hyposulphite, by which the unchanged silver salts are dissolved, and the image thus rendered insensible to the further action of light. Silver chloride is decomposed by metallic zinc, metallic silver and zinc chloride being formed.



Of the remaining silver salts, the most important are the Iodide, AgI, and the Bromide, AgBr. The Bromide is a white powder, soluble in ammonia and sodium hyposulphite, but insoluble in nitric acid. Both compounds are acted on by light, and are formed by the action of an alkaline bromide or iodide respectively on a solution of silver nitrate. Silver sulphide,  $\text{Ag}_2\text{S}$ , is black and insoluble, and is produced when sulphuretted hydrogen is passed through a solution of a silver salt. It occurs native as Silver Glance. Silver sulphate,  $\text{AgSO}_4$ , is white and crystalline, and soluble in about 90 parts of cold water.

Fulminating silver,  $\text{Ag}_2\text{C}_2\text{N}_2\text{O}_2$ , is formed by heating a solution of silver nitrate with strong nitric acid and alcohol. It crystallizes in minute needles. It is a most dangerous compound, which explodes with extreme violence by friction even when moist.

#### TESTS FOR SILVER

Silver in solution may be identified by the production of a white curdy precipitate with hydrochloric acid or a soluble chloride, which is insoluble in nitric acid, but freely soluble in excess of ammonia. With iodide of potassium, a light yellow precipitate insoluble in dilute acids and ammonia. With potassium chromate, a brick-red precipitate of silver chromate. Mixed with sodium

carbonate, and exposed on charcoal to the reducing flame of the blow-pipe, the silver compounds readily yield a white bead of metal.

## MERCURY

SYMBOL, Hg

COMBINING WEIGHT, 200

**DISTRIBUTION.**—Mercury occurs in nature in the metallic state, but by far the greater part of the metal of commerce is obtained from the native sulphide or Cinnabar,  $\text{HgS}$ , found at Almaden in Spain, at California, at Idria in Austria, and also in China and Japan. The chloride,  $\text{HgCl}$ , is also sometimes found in small quantity in nature.

**PREPARATION.**—In order to procure the metal from the native sulphide, the ore is in most cases simply subjected to a roasting process, by which the sulphur is converted into sulphurous oxide, and the mercury separates in the metallic state ( $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$ ) in the form of vapour, which is conducted into cooling chambers, and there condensed. Another plan sometimes adopted is to mix the ore with lime, and distil the mixture in iron retorts, when calcium sulphide is formed, and the metallic mercury distills over into suitable condensers ( $\text{HgS} + \text{Ca} = \text{CaS} + \text{Hg}$ ).

**PROPERTIES.**—Mercury is the only liquid metal. In its pure state it is a bright silvery liquid of specific gravity 13.59 at  $0^\circ$ , boiling at  $350^\circ$ , and freezing at  $-40^\circ$  in octahedral crystals. In the solid form it is malleable. Mercury is slightly volatile at ordinary temperatures. It does not oxidise in the air until heated to about  $300^\circ$ , when it absorbs oxygen, and is gradually converted into mercuric oxide,  $\text{HgO}$ . Mercury combines directly with sulphur, bromine, iodine, and chlorine. It is not affected by hydrochloric acid, but is freely attacked by nitric acid, and is also acted upon by hot sulphuric acid. Mercury is used in medicine, and for various purposes in the arts, such

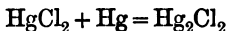
as the extraction of gold and silver from their ores, the silvering of looking-glasses, for silvering and gilding, and for the preparation of vermilion. It is also used for filling barometers and thermometers, and in the manipulation of gases in the laboratory. The alloys of mercury are termed *amalgams*.

### PRINCIPAL COMPOUNDS

Mercury forms two oxides, the mercurous  $\text{Hg}_2\text{O}$ , and the mercuric  $\text{HgO}$ , and two corresponding classes of salts.

MERCUROUS OXIDE,  $\text{Hg}_2\text{O}$ , is a black powder produced by treating a mercurous salt with excess of caustic potash. It is very unstable and is decomposed by exposure to light or heat into oxygen and metallic mercury.

MERCUROUS CHLORIDE, CALOMEL,  $\text{Hg}_2\text{Cl}_2$ , may be prepared in several ways. The ordinary method consists in heating together three parts of finely divided mercury, and four parts of mercuric chloride, in a retort—



In this reaction 271 parts by weight of mercuric chloride ( $\text{Hg} = 200, \text{Cl}_2 = 71$ ), and 200 parts of mercury yield  $271 + 200 = 471$  parts of Calomel. We can thus calculate the weights of the respective ingredients which must be taken in order to obtain a given weight of calomel. Let it be assumed for instance that an answer is desired to the following question. How much mercuric chloride and metallic mercury must be taken in order to obtain three kilograms of calomel.

First, in order to ascertain the required quantity of mercury, as 471 parts of calomel are obtained from 200 of mercury, we have—

$$\begin{array}{ccccccc} 471 & : & 3 & :: & 200 & : & x \\ & & & & x = 1.274 \text{ kilos. of Hg} \end{array}$$



Next, in order to ascertain the required amount of mercuric chloride (471 of  $\text{Hg}_2\text{Cl}_2$  requiring 271 of  $\text{HgCl}_2$ )—

$$471 \quad : \quad 3 \quad :: \quad 271 \quad : \quad x$$

$$x = 1.726 \text{ kilos. of } \text{HgCl}_2$$

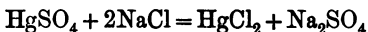
Calomel may also be prepared by precipitation, as when a solution of sodic chloride is added to a solution of mercurous nitrate or sulphate, thus— $\text{Hg}_22\text{NO}_3 + 2\text{NaCl} = \text{Hg}_2\text{Cl}_2 + 2\text{NaNO}_3$ . As prepared by the first process, the mercurous chloride must be washed in order to free it from the soluble mercuric chloride. Mercurous chloride is a yellowish white, insoluble powder, decomposed by alkalis. Black wash is made by adding calomel to lime water, when the mercury is precipitated as the black sub-oxide.

MERCUROUS NITRATE,  $\text{Hg}_22\text{NO}_3$ , is formed by acting on an excess of mercury with cold nitric acid, nitric oxide gas being evolved. It is decomposed by water into an insoluble basic, and an acid soluble salt.

MERCURIC OXIDE.—Red oxide of mercury,  $\text{HgO}$ , is formed by heating metallic mercury in the air to a temperature of about  $300^\circ$  ( $\text{Hg} + \text{O} = \text{HgO}$ ). As thus produced it is a heavy, red, crystalline powder, insoluble in water. Mercuric oxide may also be prepared by heating mercuric nitrate, or by dissolving this salt in water and adding potassium or sodium hydrate, it is then precipitated as a yellow powder. Mercuric oxide becomes black on exposure to a moderate heat, regaining its original colour on cooling. By exposure to a higher temperature it is resolved into oxygen and metallic mercury.

MERCURIC CHLORIDE, or Corrosive Sublimate,  $\text{HgCl}_2$ , is formed when metallic mercury is heated in chlorine, and also by heating a mixture of equal parts of mercuric sulphate and sodium chloride in a retort, mercuric

chloride distilling over, and sodium sulphate remaining as a residue—



Mercuric chloride is soluble in water, especially if a little hydrochlorate of ammonia is added. It is also soluble in ether, and in alcohol; ether removes it from its watery solution, an important fact when testing for this substance. It crystallises in needles or octahedra, fuses at  $265^\circ$ , and boils at  $295^\circ$ . It has a nauseous metallic taste, and is very poisonous.

MERCURIC NITRATE,  $\text{Hg}_2\text{NO}_3$ , is formed by acting on mercury with an excess of nitric acid, or by dissolving mercuric oxide in the acid.

MERCURIC SULPHATE,  $\text{HgSO}_4$ , is formed by heating mercury with an excess of sulphuric acid, as long as sulphurous oxide is evolved—



It is a white crystalline salt, decomposed by water into a yellow subsulphate, which precipitates, and a soluble acid salt.

MERCURIC SULPHIDE,  $\text{HgS}$ , found native as cinnabar, is formed as a black precipitate by the action of sulphuretted hydrogen on a solution of a mercuric salt. When sublimed the sulphide has a red colour, and is known as vermilion. It is used extensively as a paint, and is prepared for commercial purposes by carefully subliming a mixture of sulphur and metallic mercury.

FULMINATING MERCURY.—When mercury is dissolved in nitric acid, in the proportion of one part of the metal to twelve parts of the acid, the solution allowed to cool, mixed with eleven parts of alcohol, and the mixture heated in the water bath, mercuric fulminate  $\text{HgC}_2\text{N}_2\text{O}_2$  is formed. The compound separates in the crystalline form as the solution cools. It is generally met with as white, silky, needle-shaped crystals, which

when heated to  $186^{\circ}$ , or when forcibly struck, detonate with great violence.

#### TESTS FOR MERCURY

Mercury compounds are readily reduced by heating them in a closed tube with sodium carbonate, the metal forming silvery globules on the side of the tube. In solution mercury yields a black sulphide with sulphuretted hydrogen insoluble in nitric acid. Mercuric compounds yield no precipitate with sodium chloride. A scarlet precipitate of mercuric iodide,  $\text{HgI}_2$ , is formed with potassium iodide, soluble in excess of the reagent, and a dark red chromate with potassium chromate. Mercurous compounds yield a white precipitate of calomel with sodium chloride, and a black precipitate of mercurous oxide with potassium hydrate.

### COPPER

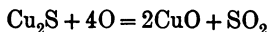
SYMBOL, Cu

COMBINING WEIGHT, 63.5

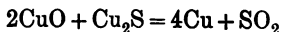
**DISTRIBUTION.**—Copper is a widely diffused metal, and is met with in nature, both in the metallic and combined state. Native metallic copper has been found on the southern shores of Lake Superior in masses of as much as 400 tons in weight. The metal of commerce is, however, generally procured from the different copper ores, the chief of which are copper pyrites, a double sulphide of iron and copper,  $\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$ , copper sulphide,  $\text{Cu}_2\text{S}$ , called copper glance; the carbonate or malachite,  $\text{CuCO}_3 + \text{CuH}_2\text{O}_2$ , and cuprous oxide,  $\text{Cu}_2\text{O}$ . Copper ores abound in Cornwall, Australia, and America.

**PREPARATION.**—Metallic copper is extracted from its ores to a large extent in Swansea, which is the principal seat in Britain of copper smelting. The treatment of the ore is a somewhat complicated operation, and is divided into several stages. Copper pyrites is the principal source of the metal. The ore is broken into

small pieces and calcined, by which the arsenic and a portion of the sulphur is expelled. The calcined mass is then smelted in a reverberatory furnace, with the addition of some slag from previous operations, and occasionally some fluor spar is added. The result of this treatment is that a large portion of the iron present is converted into a fusible silicate, and a comparatively pure copper sulphide is produced. This is run off into a cistern of cold water, by which it becomes granulated, and is called "*mat*" or "*coarse metal*." The coarse metal is then calcined, by which the iron sulphide is more or less completely converted into oxide, the copper sulphide remaining practically unchanged. This compound is then smelted with slag, by which the iron is separated, and the copper sulphide is left in a purer condition. The copper sulphide is then calcined to remove a portion of the sulphur, the copper being left as oxide—



When a portion of the copper sulphide is thus converted into oxide, the doors of the furnace are closed to exclude air, and the oxide and unchanged sulphide react on each other to form sulphurous oxide and metallic copper thus—



The copper thus obtained is purified by roasting, which carries off traces of arsenic and sulphur, and effects the oxidation of the small quantities of other metals present. The metal is now comparatively pure, but contains traces of suboxide of copper, which are removed by a process called "*poling*." The metal is remelted and stirred about with a pole of green wood, the surface of the fused material being covered with a layer of powdered charcoal or anthracite. The combustible gases evolved from the green wood have the effect of abstracting the oxygen from the suboxide of copper,

and reducing it to the metallic state. The removal of the suboxide is necessary, because minute traces of it in metallic copper materially interfere with the malleability of the metal.

**PROPERTIES.**—Copper is a metal of specific gravity 8·9, and having a red colour. It is capable of being hammered or rolled into sheets, or drawn into fine wire with facility. It is one of the best known conductors of heat and electricity. Heated in the air it oxidises to cupric oxide,  $\text{CuO}$ , and it melts at a bright red heat. Copper does not oxidise in pure air, and does not decompose water even at a red heat. Copper is extensively used in the arts, both in the pure state and for the production of alloys, the principal of which are brass, composed of two thirds copper and one third zinc; bronze, containing 91 parts copper, 6 of zinc, 2 of tin, and one of lead; and gun metal, containing 90 of copper to 10 of tin. Copper is diatonic.

#### PRINCIPAL COMPOUNDS

Copper forms two oxides,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ; the former of these is called cuprous oxide, and the latter cupric oxide; and there are two classes of corresponding salts, the cuprous and cupric.

**CUPROUS OXIDE,  $\text{Cu}_2\text{O}$ .**—This compound occurs native as red or ruby copper ore, and is met with in octahedral crystals. If to a solution of copper sulphate is added some rochelle salt, and subsequently some potassium hydrate, a deep blue liquid will be obtained, which on boiling with grape sugar deposits cuprous oxide as a powder of a dull red colour. This oxide is also formed by heating equivalent quantities of copper filings and cupric oxide ( $\text{Cu} + \text{CuO} = \text{Cu}_2\text{O}$ ). Cuprous oxide is used to impart a fine ruby red colour to glass. It forms colourless salts with acids, which have a tendency to absorb oxygen from the air, and pass into the corresponding cupric compounds.

CUPROUS CHLORIDE,  $\text{Cu}_2\text{Cl}_2$ , is formed by dissolving cuprous oxide in hydrochloric acid ( $\text{Cu}_2\text{O} + 2\text{HCl} = \text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O}$ ), by digesting metallic copper with cupric chloride ( $\text{CuCl}_2 + \text{Cu} = \text{Cu}_2\text{Cl}_2$ ), or by treating equivalent quantities of copper and cupric oxide with hydrochloric acid ( $\text{Cu} + \text{CuO} + 2\text{HCl} = \text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O}$ ). Cuprous chloride is a white solid, insoluble in water, but soluble in hydrochloric acid. The solution thus obtained possesses the curious property of absorbing carbonic oxide gas. It is therefore of use in gas analysis.

CUPROUS SULPHIDE,  $\text{Cu}_2\text{S}$ , is found native as copper glance, and may be prepared artificially by fusing together the equivalent quantities of copper and sulphur ( $2\text{Cu} + \text{S} = \text{Cu}_2\text{S}$ ).

CUPRIC OXIDE, copper monoxide, black oxide of copper,  $\text{CuO}$ , is formed when metallic copper is heated in the air, but more conveniently by heating cupric nitrate to redness—



As thus prepared it is a black hygroscopic powder. In the hydrated state cupric oxide is precipitated as a greenish blue powder ( $\text{CuH}_2\text{O}_2$ ) by the addition of a caustic alkali to a cupric salt, such as the sulphate ( $\text{CuSO}_4 + 2\text{KHO} = \text{CuH}_2\text{O}_2 + \text{K}_2\text{SO}_4$ ). If the mixture of solution and precipitate is boiled the hydrated oxide turns black and dense from becoming anhydrous. Cupric oxide forms with acids a well defined series of compounds.

CUPRIC SULPHATE, or copper sulphate,  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ , is a salt crystallising in beautiful blue crystals belonging to the triclinic system. It is the most important of the salts of copper, and is manufactured on a large scale by dissolving copper scale (cupric oxide) in sulphuric acid,  $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$ .

If the metal is boiled with sulphuric acid, cupric sulphate is also formed, sulphurous anhydride being

evolved ( $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$ ). Crystallised cupric sulphate loses four equivalents of water at  $100^\circ$ , and at a higher temperature the remaining equivalent is expelled, the anhydrous sulphate being left as a white powder. Cupric sulphate is largely employed in the manufacture of Scheele's green, Brunswick green, and other copper pigments, and in calico printing, and electro-typing.

**CUPRIC CHLORIDE**, copper chloride,  $\text{CuCl}_2$ , is formed when copper leaf is immersed in chlorine, the union taking place with evolution of light and heat. It is also produced when cupric oxide is dissolved in hydrochloric acid,  $\text{Cu} + 2\text{HCl} = \text{CuCl}_2 + 2\text{H}$ . *Metallic* copper is scarcely acted upon by hydrochloric acid with exclusion of air. Cupric chloride forms green needle shaped crystals containing two equivalents of water; they are deliquescent, being very soluble in water and alcohol, the alcoholic solution burning with a green flame. The aqueous solution is green when concentrated, but blue when diluted. By exposure to a red heat cupric chloride loses chlorine, and is converted into cuprous chloride ( $2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + 2\text{Cl}$ ).

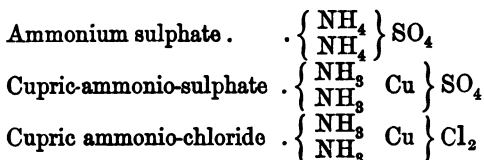
**CUPRIC NITRATE**, copper nitrate,  $\text{Cu}_2\text{NO}_3 + 6\text{H}_2\text{O}$ , is formed by dissolving copper or either of its oxides in nitric acid. It is a very soluble deliquescent salt, crystallising in blue prisms. It is soluble in alcohol.

**COPPER CARBONATE**,  $\text{CuCO}_3$ , is not known in the pure state, but a basic carbonate,  $\text{CuCO}_3 + \text{CuH}_2\text{O}_2$ , occurs native as malachite, and is formed as a green precipitate whenever an alkaline carbonate is added to a solution of a copper salt. This precipitate is used as a pigment under the name of mineral green.

**CUPRIC SULPHIDE**,  $\text{CuS}$ , is formed as a black precipitate when sulphuretted hydrogen is passed into a solution of a copper salt.

**DOUBLE SALTS OF COPPER AND AMMONIA.**—By the addition of ammonia to a solution of some of the copper salts, or by the passage of gaseous ammonia over

the solid salt, compounds are formed which may be regarded as ammonium salts, in which some of the hydrogen is replaced by the disengaged copper, thus :—



### TESTS FOR COPPER

The soluble copper salts are either green or blue, and their solutions strike a deep blue colour with excess of ammonia. The most characteristic reactions of copper in solution are the production with sulphuretted hydrogen of black sulphide when the solution is acid, a chocolate-brown precipitate of cupric ferrocyanide with yellow prussiate of potash, and green precipitate of Scheele's green with sodium arsenite. A bright iron or steel article, placed in an acid solution containing copper, becomes red from deposition of the copper on the iron or steel; a bead of the metal is produced when a compound of copper, mixed with carbonate of soda on a piece of charcoal, is placed in the reducing flame of a blow-pipe.

### GENERAL CHARACTERISTICS OF THE GROUP

The metals of the silver group do not decompose water under any conditions. Each of the metals form two basic oxides which, except in the case of copper, are decomposed by heat. The chlorides (cuprous, mercurous, and argentic), are insoluble.

[TABLE



*Table showing the Leading Characteristics of the Principal Compounds of the Metals of the Silver Group, together with their Distinctive Tests :—*

OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDES	DISTINCTIVE TESTS
<p>The suboxide, <math>\text{Ag}_2\text{O}</math>, is a black insoluble powder. The monoxide, <math>\text{Ag}_2\text{O}</math>, is brown and insoluble, and is a strong base.</p>	<p>Black and insoluble.</p>	<p><math>\text{AgSO}_4</math> is white and crystalline, and soluble in about 90 parts of cold water.</p>	<p><math>\text{AgNO}_3</math> forms transparent tabular crystals, which are anhydrous, and are soluble in an equal weight of cold water.</p>	<p><math>\text{AgCl}</math> is white and insoluble in water and acids, but soluble in ammonia. When fused, it forms a semi-transparent mass resembling horn.</p>	<p>Solutions of <math>\text{Ag}</math> are colourless, and are chiefly characterised by yielding a white curdy precipitate of <math>\text{AgCl}</math> with <math>\text{HCl}</math>, or a soluble chloride. This precipitate is insoluble in nitric acid, but soluble in <math>\text{NH}_3</math>, and in solutions of alkaline hyposulphites. <math>\text{Ag}</math> in solution also gives a red precipitate with potassium chromate, and a yellowish-white precipitate with <math>\text{KI}</math>.</p>

SILVER

Table—Continued

OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDES	DISTINCTIVE TESTS
<p>Mercurous oxide, <math>\text{Hg}_2\text{O}</math>, is a black unstable powder, easily decomposed by exposure to light or heat. Mercuric oxide, <math>\text{HgO}</math>, is a heavy, red, crystalline powder, insoluble in water.</p>	<p>Black and insoluble, but when red, when sublimed.</p>	<p><math>\text{HgSO}_4</math> is a white crystalline salt, decomposed by water, by the action of which a yellow insoluble subsulphate and a soluble acid salt is formed.</p>	<p>Mercurous nitrate, <math>\text{Hg}_2(\text{NO}_3)_2</math>, and mercuric nitrate, <math>\text{Hg}(\text{NO}_3)_2</math>, are both crystalline salts, the strong solutions of which are decomposed by dilution, in basic salts being formed.</p>	<p>Mercurous chloride (Calomel), <math>\text{Hg}_2\text{Cl}_2</math>, is a white powder, insoluble in water, and blackened by ammonia. Mercuric chloride (Corrosive sublimate), <math>\text{HgCl}_2</math>, is a salt, crystallising in needles, and soluble in water, alcohol, and ether.</p>	<p>Mercury compounds, when heated in a tube with sodium carbonate, yield a sublimate of the metal, which collects on the side of the tube in silvery globules. Solutions of Hg are colourless, and give a red chromate with solution of potassium chromate, and a brilliant scarlet precipitate of iodide with solution of KI. Mercurous compounds in solution give a white precipitate of <math>\text{Hg}_2\text{Cl}_2</math>, with a soluble chloride, which is blackened by <math>\text{NH}_3</math>.</p>

MERCURY

Table—Continued

OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDES	DISTINCTIVE TESTS
<p>Cuprous oxide, <math>\text{Cu}_2\text{O}</math>, is an insoluble powder, of a fine red colour.</p> <p>Cupric oxide, <math>\text{CuO}</math>, is a heavy, black, insoluble powder.</p>	<p>Black and insoluble.</p>	<p><math>\text{CuSO}_4 + 5\text{H}_2\text{O}</math> is a blue crystalline salt, freely soluble in water.</p>	<p><math>\text{Cu}_2\text{NO}_3 + 6\text{H}_2\text{O}</math> is a blue deliquescent salt, crystallising in prisms, and is very soluble in water and alcohol.</p>	<p>Cupric chloride, <math>\text{CuCl}_2 + 2\text{H}_2\text{O}</math>, forms green needle-shaped crystals, which are very deliquescent, and soluble in water and alcohol.</p> <p>Cuprous chloride, <math>\text{Cu}_2\text{Cl}_2</math>, is a white powder, insoluble in water.</p>	<p>Solutions of Cu are generally blue, but the concentrated chloride is green. They are characterised by striking a deep blue with excess of <math>\text{NH}_3</math>, giving a greenish-blue precipitate of hydrate with <math>\text{KHO}</math>, and yielding a chocolate-brown precipitate with solution of potassium ferrocyanide. They also yield with sodium arsenite a precipitate of Scheele's green.</p>

COPPER

*Table showing the Action of Heat on the Principal Compounds of the Metals of the Silver Group :—*

	OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDE
Silver	All the oxides of silver are decomposed by a strong heat into oxygen and metallic silver.	$\text{Ag}_2\text{S}$ is converted by ignition in air into sulphate.	Melts at a comparatively low temperature, and decomposes at a higher temperature, leaving metallic silver.	Melts at $219^\circ$ to a clear colourless liquid.	$\text{AgCl}$ melts at $260^\circ$ without decomposition to a transparent yellowish liquid, and volatilises at a very high temperature.
Copper	$\text{CuO}$ melts at a full red heat without decomposition.	At a red heat, in the presence of air, the sulphides of copper are decomposed, $\text{SO}_2$ being given off and $\text{CuO}$ remaining.	The crystallised salt evolves four equivalents of water at $100^\circ$ , and the remaining equivalent at $300^\circ$ , leaving the anhydrous compound as a white mass, which is decomposed at a bright red heat, evolving $\text{SO}_2$ and $\text{O}$ , and leaving $\text{CuO}$ .	Copper nitrate melts in its water of crystallisation at a comparative low temperature, and at a red heat is decomposed, leaving $\text{CuO}$ and evolving $\text{NO}_2$ .	Cupric chloride $\text{CuCl}_2$ melts at a red heat, giving off half its chlorine, and becoming cuprous chloride $\text{Cu}_2\text{Cl}_2$ . Cuprous chloride $\text{CuCl}$ melts somewhat below a red heat, evolving white vapours.

Table—Continued

	OXIDES	SULPHIDE	SULPHATE	NITRATE	CHLORIDE
Mercury	HgO and Hg <sub>2</sub> O are both decomposed by heat into oxygen and metallic mercury.	HgS sublimes when heated strongly in a closed vessel. When heated in the air SO <sub>2</sub> is formed and metallic mercury passes off in vapour.	Sulphate of mercury bears an incipient red heat without alteration, but melts at a higher temperature to a brown liquid, and finally completely volatilises.	All the nitrates of mercury are decomposed by heat evolving nitrogen oxides and leaving HgO.	Mercurous chloride or calomel, HgCl, entirely volatilises below a red heat without previous fusion. Mercuric chloride or corrosive sublimate, HgCl <sub>2</sub> , melts at 265°, boils at 295°, and volatilises even more easily than calomel.

## THE GOLD GROUP

## GOLD

SYMBOL, Au

COMBINING WEIGHT, 197

DISTRIBUTION.—Gold is always found in a metallic state in nature, principally in the form of small particles in the alluvial sand of certain rivers, and in auriferous quartz. It is also occasionally met with in larger detached masses called “nuggets.” Most native gold contains a little silver and copper. The Australian gold is the purest variety found.

PREPARATION.—The metal is procured by washing the sand containing it in a stream of water, the foreign materials are then carried away, and the metal, owing to its superior density, is left. Gold quartz is crushed by machinery, and afterwards subjected to the washing process. The metal has, in most cases, to be separated from all earthy impurities by agitation with mercury, when an amalgam is formed, which, on distillation, leaves the gold. Auriferous quartz is sometimes treated by the wet method, which consists in exposing it to the action of chlorine gas, when the metal is separated as chloride. Gold is separated from silver and copper by boiling with sulphuric acid, when the two last named metals are dissolved. This process is called parting. In order to render gold thoroughly malleable, it is necessary to free it from all traces of such foreign metals as antimony, lead, etc., and this is frequently effected on a large scale by treating the melted metal with chlorine gas, when the baser metals are converted into chlorides and volatilised. Perfectly pure gold is best prepared by adding a solution of ferrous sulphate to a solution of the chloride, when the ferrous sulphate is oxidised to a ferric salt, and the *gold precipitates as a fine powder.*

**PROPERTIES.**—Pure gold is a rich yellow metal, possessing great lustre, and having a specific gravity of 19.3. It is very ductile, and is also the most malleable of the metals, being capable of being beaten into leaves only 1-280,000th of an inch in thickness. Gold does not oxidise in the air at any temperature, neither is it tarnished by the action of sulphuretted hydrogen, but it combines directly with chlorine and bromine at ordinary temperatures, and when previously heated, with phosphorus. Gold is not attacked by any of the ordinary acids, selenic acid being the only one which dissolves it, a mixture of concentrated hydrochloric and nitric acid (aqua regia) will, however, dissolve it.

Alloys of gold and copper are much used for the manufacture of jewellery. The gold coin of the realm contains 22 parts of gold to 2 of copper. Alloys of gold and copper are described as being of so many carats according to the number of parts of gold in 24 parts of the alloy.

### PRINCIPAL COMPOUNDS

Gold forms two oxides, the suboxide,  $\text{Au}_2\text{O}$ , and the trioxide,  $\text{Au}_2\text{O}_3$ , and two chlorides.

*Gold Oxides.*—The suboxide or aurous oxide,  $\text{Au}_2\text{O}$ , is a green powder obtained by the action of cold potash solution on auric chloride. The trioxide, or auric oxide,  $\text{Au}_2\text{O}_3$ , is prepared by digesting a solution of the trichloride with magnesia or zinc oxide, and treating the precipitate with nitric acid to dissolve the zinc or magnesia. The oxide is a brownish-black powder, decomposed by exposure to direct sunlight into oxygen and metallic gold. This decomposition is also effected by a temperature of  $250^\circ$ . Gold trioxide unites with bases to form aurates.

*Gold Chlorides.*—The monochloride, or aurous chloride,  $\text{AuCl}$ , is found as a white insoluble mass by exposing auric chloride to a temperature of about the

melting point of tin. The trichloride or auric chloride,  $\text{AuCl}_3$ , is the most important compound of gold. It is formed when the metal is treated with chlorine, or with aqua regia. It forms a crystalline compound with hydrochloric acid ( $\text{AuCl}_3\text{HCl}$ ), and similar compounds with the alkaline chlorides. Auric chloride is deliquescent, very soluble in water, and dissolves also in ether. By acting on a solution of gold with excess of ammonia, a brown compound is precipitated, called fulminating gold, which in the dry condition explodes, either by percussion or by heating to  $100^\circ$ .

#### TESTS FOR GOLD

The compounds of gold in solution may be identified by giving a precipitate of the metal (in the absence of nitric acid) by the addition of ferrous sulphate, and by the production of a precipitate known as purple of Cassius on the addition of a mixture of perchloride and protochloride of tin.

#### PLATINUM

SYMBOL, Pt

COMBINING WEIGHT, 197.4

**DISTRIBUTION.**—Platinum, like gold, is found in nature only in the metallic state. In this condition it is, however, not pure, but associated as an alloy with five other metals, viz., rhodium, iridium, palladium, osmium, and ruthenium. This alloy is comparatively rare, occurring, as a rule, in small flattened steel grey grains. The chief locality from which it is obtained is the Ural Mountains, but small quantities have been also obtained from Brazil, Australia, California, Borneo, and Peru.

**PREPARATION.**—Metallic Platinum was formerly prepared by treating the native alloy, first, with nitric, and then with hydrochloric acid, by which traces of



iron, copper, &c., were removed, and finally, by aqua regia, which dissolved the platinum and the other metals associated with it. The solution so obtained was mixed with ammonium chloride, by which the platinum was precipitated in the form of a yellow compound, the double chloride of platinum and ammonium. When heated, this compound leaves metallic platinum as a spongy mass. Latterly, a more expeditious process for preparing platinum has been employed, in which the native ore is fused with lead, and the alloy with lead thus obtained is subjected to cupellation, by which the metallic platinum is left as a spongy mass. By subjecting this mass to the flame of the oxy-hydrogen blow-pipe in a small lime furnace, any remaining traces of other metals are volatilised and the platinum fused. The metal thus obtained contains some iridium and rhodium, which, however, do not interfere with its useful applications.

**PROPERTIES.**—Platinum is a silver white metal of specific gravity, 21.5. It is of the same hardness as copper, and equals iron in ductility, tenacity, and malleability. It is infusible at any temperature short of that attainable by the oxy-hydrogen blow-pipe. It does not oxidise in the air, either at ordinary or at elevated temperature, and is not attacked by any single acid; it is, however, slowly dissolved by aqua regia, and at a red heat is attacked by alkaline hydrates and nitrates. It readily forms fusible alloys with such metals as lead, antimony, bismuth, tin, and zinc, and on this account care should be taken not to heat the easily reducible compounds of these metals in a platinum vessel.

The chief uses of platinum are for the manufacture of crucibles, and vessels for chemical purposes, for which it is admirably adapted, and for stills used for the concentration and distillation of pure sulphuric acid. In the spongy form platinum possesses a capability of condensing gases within its pores, and of

frequently causing their union. Thus, when a mass of spongy platinum is placed in a jet of hydrogen and oxygen, it becomes red hot, and causes the ignition of the gases.

### PRINCIPAL COMPOUNDS

Platinum forms two oxides; the monoxide, or platinous oxide,  $\text{PtO}$ , and the dioxide, or platinic oxide,  $\text{PtO}_2$ .

Platinous oxide is obtained in the hydrated form as a black powder by digesting platinous chloride with caustic potash. Platinic oxide is obtained as hydrate by the action of a limited amount of caustic potash on platinic chloride. It has a rusty red colour. Both oxides are readily reduced to the metallic state by simple ignition.

Two chlorides of platinum are known. The platinous salt,  $\text{PtCl}_2$ , being an insoluble olive green powder, produced by heating platinic chloride to about  $200^\circ$ . Platinic chloride,  $\text{PtCl}_4$ , is an orange yellow deliquescent salt, produced by dissolving the metal in aqua regia. This salt is the most important of the platinum compounds, it is very soluble in water, and is remarkable for forming double chlorides with ammonia, and most of the alkali metals. The compounds with ammonium and potassium are insoluble in water, and have the formula,  $2\text{NH}_4\text{Cl}, \text{PtCl}_4$ , and  $2\text{KCl}, \text{PtCl}_4$ , respectively. They are isomorphous. The sodium compound is soluble, and has the composition,  $2\text{NaCl}, \text{PtCl}_4 + 6\text{H}_2\text{O}$ . Platinic chloride also forms double salts with many organic chlorides, and when acted on by ammonia forms some remarkable compounds of a basic nature, containing Nitrogen, Hydrogen, and Platinum. These compounds may be regarded as molecules of ammonium, in which part of the hydrogen is replaced by platinum. They form a well-defined series of salts.

The metals associated with platinum, viz., rhodium, iridium, *osmium*, and palladium, are comparatively rare,

and the description of their preparation and compounds scarcely comes within the scope of the present work.

#### GENERAL CHARACTERISTICS OF THE GROUP

These metals do not decompose water under any conditions, and are distinguished from all the preceding metals by the fact of being unaffected by the single action of either nitric or hydrochloric acid. Their oxides are all reduced by simple exposure to heat, and together with silver and mercury they constitute the so-called *noble* metals.

*Table showing the leading characteristics of the principal compounds of the Metals of the Gold Group, together with their distinctive tests:—*

	SULPHIDE	OXIDES	CHLORIDES	DISTINCTIVE TESTS
Gold	Black and insoluble.	Aurous oxide, $\text{Au}_2\text{O}_3$ , is a green insoluble powder. Auric oxide, $\text{Au}_2\text{O}_3$ , is a brownish black insoluble powder.	$\text{AuCl}_3$ , Aurous chloride, is white and insoluble in water. Auric chloride, $\text{AuCl}_3$ , forms yellow deliquescent crystals, very soluble in water, and which also dissolve in ether.	The solutions of gold are yellow in colour, and yield with oxalic acid, or with $\text{FeSO}_4$ , a precipitate of metallic gold. They give also a characteristic purple precipitate on the addition of a mixture of perchloride and protochloride of tin.
Platinum	Black and insoluble.	Platinous oxide, $\text{PtO}$ , is a black powder. Platinic oxide, $\text{PtO}_2$ , is in the hydrated state a brown powder. Both oxides are insoluble in water.	$\text{PtCl}_2$ , Platinous chloride, is olive green and insoluble in water. Platinic chloride, $\text{PtCl}_4$ , is an orange yellow, deliquescent salt very soluble in water, and also dissolving in alcohol and ether.	Solutions of platinum are yellow, and are chiefly characterised by affording double compounds with ammonium chloride, and with potassium chloride, both of which are yellow, crystalline, and very sparingly soluble, and a corresponding sodium compound which is soluble.

*Table showing the Action of Heat on the Principal Compounds of the Chief Metals of the Gold Group*

	OXIDES	CHLORIDES
Gold	<p>The oxides of both gold and platinum are reduced to the metallic state by exposure to a strong heat.</p>	<p>The tetrachloride <math>\text{AuCl}_3</math> loses two equivalents of chlorine at <math>185^\circ</math>, and is converted into aurous chloride, <math>\text{AuCl}</math>; when exposed to a higher temperature, all the chlorine is given off and metallic gold is left.</p>
Platinum		<p>Platinic chloride, <math>\text{PtCl}_4</math>, is converted into platinous chloride, <math>\text{PtCl}_2</math>, by exposure to a moderate temperature, and when more strongly heated is decomposed leaving metallic platinum.</p>

## QUALITATIVE ANALYSIS

The methods in use for the detection of the presence of the various elements and their compounds vary with the nature and condition of the substance to be examined. The first step in the systematic examination of any substance is to bring it into solution, if it is not already in that condition. A general distinction may therefore be made at the commencement of the subject between the examination of fluids and that of solids. In the case of the former, tests may be directly applied in order to ascertain what substances are present; but, in the case of the latter, useful information may frequently be gained by the effect of the application of heat, and by a systematic trial of the action of different *solvents*. In the following remarks and tables, the *directions* are confined simply to the detection of the

compounds occurring in *inorganic* chemistry, the identification of *organic* substances requiring more advanced knowledge in analysis than can be given in an elementary work.

Starting with the examination of simple compounds, containing an acid and a base, much information may be gained by noting the colour of the solid or liquid, and in the case of solids, by observing the general physical characteristics, and the action of heat and of solvents.

In the following description and tables pp. is frequently used as an abbreviation for precipitate.

## SECTION I.—PRELIMINARY EXAMINATION

1. *The Substance is Liquid.*
2. *The Substance is Solid.*

### 1. THE SUBSTANCE IS LIQUID

*Note colour of solution*, remembering the characteristic colours of many metallic compounds, and that in the event of the liquid being colourless, it is probable that such compounds are not present.

Ascertain the reaction of the liquid to red and blue litmus paper; this will tell at once whether the solution contains a neutral, an alkaline, or an acid salt, and will afford a guide to the subsequent analysis. The systematic examination is then effected as in section 2.

### 2. THE SUBSTANCE IS SOLID

*Action of heat.*—Reduce the substance to powder, and place a small portion in the centre of a small tube of hard glass; now hold the tube in an inclined position in the flame of a Bunsen burner. If fusion takes place, it indicates the presence of a fusible salt, such as an

alkaline nitrate or chlorate; if watery vapour is at the same time expelled, the presence of salts containing water of crystallisation is shewn. If sulphur or a sulphide is present an odour of sulphurous acid will be evolved, while if a garlic like odour is given off, arsenic may be suspected. In the latter case a crystalline sublimate of white octahedral crystals will be formed. If a white amorphous sublimate appears, salts of ammonia, may be present, or volatile metallic compounds, such as those of mercury or cadmium.

A further portion of the substance is mixed with a little carbonate of soda, and exposed on charcoal to the action of the inner blow-pipe flame. Deflagration will betray the presence of a nitrate or chlorate, while the formation of a metallic globule will show the presence of a compound of an easily reducible metal. In searching for metallic globules the fused mass should be crushed and rubbed in a mortar with a little water. Lead may be recognised by its softness, and by its marking white paper, in this case a yellow incrustation will be observed on the charcoal. The presence of tin is accompanied with a slight white incrustation, and the metallic bead is white and malleable, but does not mark paper, and emits a peculiar noise when crushed between the teeth. Antimony yields a brittle white bead accompanied with abundant white incrustation. Bismuth gives a semi-malleable bead, distinguished from lead by its not marking paper, and accompanied with abundant yellow incrustation. Copper, gold, and silver, may be recognised by their respective colours. Zinc and Cadmium yield no metallic globules, but are characterised, the former by yielding an incrustation, which is yellow when hot, and which turns white on cooling, and the latter by affording a brown incrustation,

Further information may be obtained by fusing a further portion of the material mixed with borax to the blow-pipe flame, on a small loop of platinum wire. The following table shows the principal reactions:—

	OUTER BLOW-PIPE FLAME	INNER BLOW-PIPE FLAME
Chromium	Green bead	The same
Copper	Green bead	Dull red bead
Iron	Yellowish bead	Green bead
Nickel	Reddish yellow bead	Gray bead
Manganese	Amethystine bead	Colourless bead
Cobalt	Bright blue bead	The same

Action of solvents.

*Boil with distilled water.*

THE SUBSTANCE DISSOLVES	THE SUBSTANCE DOES NOT DISSOLVE
It can only consist of one of the soluble compounds. Note colour of solution and reaction to test paper.	It may be any of the insoluble compounds, including such a substance as an earthy carbonate or insoluble metallic oxide, etc.

*Treat with dilute nitric acid.*

THE SUBSTANCE DISSOLVES		THE SUBSTANCE DOES NOT DISSOLVE
WITH EFFERVESCENCE	WITHOUT EFFERVESCENCE	
Presence of a carbonate or sulphide, the odour of $H_2S$ furnishing a point of distinction in the latter case.	Absence of a carbonate or sulphide.	It probably consists of one of the more insoluble metallic compounds, or may be an earthy silicate.



*Treat with ammonia in the cold.*

IT DISSOLVES	IT DOES NOT DIS- SOLVE BUT TURNS BLACK	IT IS UNAFFECTED
The substance is AgCl.	The substance is HgCl.	Absence of AgCl, or HgCl.

Boil with strong HCl, and subsequently with aqua regia, for some time; if the substance is still insoluble it probably consists of an earthy silicate, or some other insoluble compound requiring fusion with an alkali to bring it into solution, and requiring special methods of analysis, for an account of which the student is referred to the larger text books on analysis.

## SECTION II.—SYSTEMATIC EXAMINATION

The systematic examination of a substance is always effected on the solution, and generally by the use of liquid reagents. It will be best to divide this portion of the subject into two parts, the first of which describes the treatment to be adopted where a simple compound is present, containing only a base and an acid; while the second is devoted to the system of examination suited for more complex mixtures, in which many bases and acids may be present.

## PART I.

For the analysis of a solution known to contain only one base and one acid.

## EXAMINATION FOR THE BASE

TABLE I.

Add HCl to slight excess.

A PRECIPITATE IS PRODUCED	NO PRECIPITATE
Presence of Ag., Pb., or Hg (as a mercurous salt).	Pass on to Table II.

Add ammonia.

Precipitate dissolves—*Silver*.

Precipitate turns black—*Mercury*.

It is not affected—*Lead*.

Confirm presence of lead by adding dilute sulphuric acid to a portion of original solution, *white pp.* and potassium chromate to another portion, *yellow pp.*

*Note.*—If a hyposulphite is present the solution will, after the addition of the HCl, become gradually turbid from the separation of sulphur, and will evolve an odour of  $\text{SO}_2$ . This turbidity is, however, not likely to be confounded with the production of a precipitate of a metallic compound.

TABLE II.

Pass a current of  $\text{H}_2\text{S}$  through the solution in which HCl has occasioned no precipitate. If no precipitate is produced pass on to Table III.

*A precipitate is produced.*

1. The pp. is yellow. Presence of *Cadmium, Arsenic, or Tin* (as a stannic salt). Add  $\text{NH}_3$ , pp. is not dissolved, cadmium. Precipitate dissolves, arsenic, or tin. Add  $\text{NH}_3$  to original solution, a white pp. indicates tin. If no pp. confirm presence of As. by special tests.

2. The precipitate is orange. *Antimony*—the pp. will be soluble in ammonium sulphide.

3. The precipitate is brown. Tin (as a stannous salt). Confirm by adding  $\text{HgCl}_2$  to a portion of the original solution which will give a white pp.

4. The precipitate is black. *Lead, Bismuth, Copper, Mercury, Gold, or Platinum*. If Cu is present the original solution will be blue, while Au. or Pt in solution are yellow. Test portions of original solution, (1) with dilute sulphuric acid, white pp. indicates Pb; (2) with  $\text{NH}_3$  in excess, a greenish blue pp. dissolving to a blue liquid, Cu.; (3) with excess  $\text{KHO}$ , a yellow pp., Hg; (4) with a mixture of  $\text{SnCl}_2$  and  $\text{SnCl}_4$ , purple pp., Au; (5) with  $\text{NH}_4\text{Cl}$ , yellow crystalline pp., Pt. (6) Concentrate a portion of original solution, and afterwards add excess of water, white pp. Bi. In all cases confirm by further special tests.

### TABLE III.

To the solution which has failed to give a precipitate with  $\text{H}_2\text{S}$ , add ammonia, ammonium chloride and ammonium sulphide. If no precipitate is produced pass on to table IV.

*A precipitate is produced.*

1. It is *white*—may be Al or Zn, add  $\text{NH}_3$  to a portion of original solution, a white pp. will be formed which will be soluble in excess of  $\text{NH}_3$  if Zn is present, insoluble in the case of Al.

2. It is *green*—dissolve in potash and boil, pp. reappears Cr. Confirm by fusing pp. with a little potassium nitrate, dissolving and testing solution for chromic acid with lead acetate.

3. Precipitate is *flesh coloured*, Mn. Confirm by blow-pipe test.

4. Precipitate is *black*, Fe, Ni, or Co, may be present. Add potash in excess to a portion of original solution. A dirty green or reddish brown pp. indicates Fe (confirm with ferrocyanide of potassium). A light green pp. which does not change colour shows Ni, while a sky blue pp. becoming of a reddish colour on the application of heat indicates Co (confirm by blow-pipe test).

TABLE IV.

*To the solution in which ammonium sulphide has given no precipitate, add ammonium carbonate :—*

A PRECIPITATE IS PRODUCED	NO PRECIPITATE
Ba, Sr, or Ca, add $\text{CaSO}_4$ to original solution, immediate pp. shows Ba, if only after a time, Sr, if none, Ca is present. Confirm by adding oxalate of ammonia to original solution white pp. confirm distinction between Ba and Sr by hyposulphite test.	Add sodium phosphate, and shake briskly, a white crystalline pp. Mg. If no precipitate—pass on to table V.

TABLE V.

If all previous treatment has failed to indicate the substance which is present, the original solution can only contain one of the alkalis. Heat a little of the solution with KHO, when the presence of  $\text{NH}_3$  will be recognised by its odour, and by the production of white fumes, with a glass rod moistened with HCl. If  $\text{NH}_3$  is absent, test a further portion of the original solution for K, with tartaric acid in excess, and another portion with  $\text{PtCl}_4$ . If no precipitate is produced, only *soda can be present*.

*Detection of the Acid.*

As this portion of the examination is comparatively simple, and as the method of analysis is very similar, whether a simple substance or a mixture of substances is being tested, no distinct method of analysis will be given here, but the student is referred to Part II., Section II., *detection of Acid*. It may be remarked, however, that the preliminary examination will probably have revealed the presence or absence of carbonic, hydrosulphuric and hyposulphurous acids, as well as of the acids of arsenic. The detection of the base will also have probably afforded a clue to what acid is likely to be present, from the knowledge the student is presumed to possess of the principal compounds formed by each metal.

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## PART II.

For the analysis of complex mixtures containing more than one acid and base.

*Detection of the Bases.*

## TABLE I.

Add HCl in excess to the solution. If no pp. is produced, pass on to Table II.

A pp. is produced. Pb, Ag, and Hg (as a mercurous salt), may be present. Separate the liquid by filtration, and put pp. into a test tube, boil with distilled water and filter.

EXAMINATION OF FILTRATE	EXAMINATION OF THE RESIDUE.
<p>This will contain any Pb that may be present, and on cooling will deposit crystals of <math>\text{PbCl}_2</math>. The solution will give a white pp. with dilute <math>\text{H}_2\text{SO}_4</math>, and a yellow pp. with <math>\text{K}_2\text{CrO}_4</math>. If none of these reactions occur Pb is absent.</p>	<p>Transfer to a test tube, and add <math>\text{NH}_3</math>. Blackening indicates Hg. Dilute mixture, filter, and add excess of <math>\text{HNO}_3</math> to filtrate, a white curdy pp. indicates Ag.</p>

TABLE II.

The solution which has given no pp. with  $\text{HCl}$ , or the solution from which the pp. by  $\text{HCl}$  has been removed by filtration is now slightly diluted, and a current of  $\text{H}_2\text{S}$  passed until the liquid smells strongly of the gas.

*No precipitate is produced.* Pass on to table III.

*A precipitate is formed.*  $\text{Cu}$ ,  $\text{Sn}$ ,  $\text{Sb}$ ,  $\text{As}$ ,  $\text{Bi}$  and  $\text{Cd}$  may be present. The pp. is filtered off, and the filtrate reserved for further examination. The pp. on filter is then washed, transferred to a beaker and heated for a short time with ammonium sulphide, the mixture thrown on a filter, and the insoluble residue slightly washed.

*Examination of filtrate.* Add a slight excess of  $\text{HCl}$ . If a yellow pp. of sulphur only takes place, further examination is unnecessary. If a pp. of metallic sulphide occurs, collect it on a filter and boil in a test tube for about a quarter of an hour, with a strong solution of ammonium carbonate, and then filter.

Table I.

EXAMINATION OF FILTRATE	EXAMINATION OF RESIDUE
May contain As and Sn. Acidify with HCl, pass $H_2S$ , collect pp., and mix with a little $NaCO_3$ and potassium cyanide; divide mixture into two parts. Test one for As by reduction method, and the other for Sn by blowpipe.	May contain Sb and Sn. Wash well with weak solution of ammonium carbonate, and then dissolve in aqua regia. Add ammonium carbonate in excess, and boil. If a white residue is left, Sn is probably present; separate this residue by filtration, and apply blow-pipe test. Test filtrate by acidifying with HCl, and passing $H_2S$ ; an orange pp. shows Sb.

Table II.

*Examination of Residue Insoluble in Ammonium Sulphide*

Boil with dilute  $HNO_3$  and filter

EXAMINATION OF FILTRATE	EXAMINATION OF RESIDUE
May contain Pb, Bi, Cu, and Cd. Evaporate solution to expel excess of $HNO_3$ , and add dilute $H_2SO_4$ ; a white precipitate indicates lead. If pp. occurs, separate by filtration. Add $NH_3$ in excess to filtrate; a white pp. shows Bi. Separate by filtration, and corroborate presence of Bi by dissolving pp. in $HNO_3$ , evaporating nearly to dryness, and diluting with water; a white pp. confirms presence of Bi. The filtrate from the $NH_3$ pp. is acidified with HCl, and $H_2S$ passed; the pp. is washed, boiled with dilute $H_2SO_4$ in a test-tube, and solution filtered. To filtrate add $H_2S$ ; yellow pp. shows Cd. The residue on filter is probably $CuS$ . Dissolve in $HNO_3$ , and test with $NH_3$ , which will give a blue colour, and with potassium ferrocyanide, which will give a brown pp.	May contain Hg. Dissolve in a little aqua regia, add excess $NH_3$ , and acidify solution with HCl. A clean, bright slip of copper will be covered with a silver coating if Hg is present.

TABLE III.

To the solution in which  $\text{H}_2\text{S}$  has produced no precipitate or to the filtrate from the  $\text{H}_2\text{S}$  treatment, add  $\text{NH}_4\text{Cl}$ , then render alkaline with  $\text{NH}_3$ , and finally add excess of ammonium sulphide.

No pp. Pass on to table IV.

A precipitate is produced, Co, Ni, Fe, Au, Al, Mn, or Cr, may be present. Collect pp. on a filter and wash slightly, reserving filtrate for further treatment. Treat pp. with dilute  $\text{HCl}$ , agitate, and allow to stand for some time; if a black residue remains, either Co or Ni is present, or both. The residue may be specially tested by blow-pipe and dissolved in aqua regia and tests applied to the solution. The  $\text{HCl}$  solution is now boiled with excess of  $\text{KHO}$ , and the solution slightly diluted and filtered while still hot.

TABLE IV.

EXAMINATION OF FILTRATE	EXAMINATION OF RESIDUE
<p>Divide into two portions. To one add <math>\text{H}_2\text{S}</math> in excess; white pp. indicates Zn. To the other portion add <math>\text{NH}_4\text{Cl}</math>, and allow to stand some time; a gelatinous semi-transparent pp. indicates Al. Confirm by blow-pipe test.</p>	<p>Test a portion for Fe by solution in <math>\text{HCl}</math> and addition of potassium ferrocyanide. To ascertain whether a <i>ferrous</i> or a <i>ferric</i> salt is present, test original solution.</p> <p>A further portion is tested for Cr by fusion with <math>\text{KNO}_3</math> solution in water, addition of a little acetic acid, and finally lead acetate; yellow pp. shows Cr.</p> <p>A further portion is tested for Mn by fusion with <math>\text{NaCO}_3</math> before blow-pipe.</p>

*Note.*—If a phosphate of an alkaline earth is present in the original solution, it will be found in that portion in the last examination insoluble in  $\text{KHO}$ . A portion of the pp. should be dissolved in  $\text{HCl}$ , a little  $\text{Fe}_2\text{Cl}_6$  added, and finally sodium acetate in excess; a light-brown pp. indicates



the presence of the phosphate of an alkaline earth. If the solution is now filtered, a little  $\text{NH}_3$  added to remove excess of Fe, and again filtered, the filtrate may be examined for the alkaline earth, as described in Table V.

TABLE V.

To the solution in which all previous treatment has failed to produce a precipitate or to the filtrate from the pp. by ammonium sulphide, ammonium carbonate in excess is added.

A precipitate is produced. Ca, Ba, Sr, and Mg may be present; dissolve pp. in acetic acid. To the solution add  $\text{K}_2\text{CrO}_4$  in excess, a yellowish white pp. indicates Ba, filter, and to filtrate add dilute  $\text{H}_2\text{SO}_4$  in excess, the *immediate* formation of a white pp. insoluble in boiling  $\text{HCl}$ , indicates Sr. Filter, and to filtrate add  $\text{NH}_3$  in slight excess, and then ammonium oxalate in excess a fine white pp. shows Ca. Finally, filter, and add to filtrate sodium phosphate and  $\text{NH}_3$ , and shake briskly. A white crystalline pp. indicates Mg.

TABLE VI.

If all previous treatment has failed to produce any precipitate, only alkalis can be present. In any cases these substances must be searched for in the original solution which should be treated as follows. The presence of  $\text{NH}_3$  may be at once proved by adding  $\text{KHO}$  to a little of the original solution and applying heat when the evolution of an ammoniaal odour, the bluing of reddened litmus paper by the vapour, and the production of white fumes on the approach of a rod moistened with  $\text{HCl}$  will be conclusive evidence. The examination for K and Na must be conducted on a separate portion of the original solution. Add solution of barium hydrate in excess, heat, and filter; treat filtrate with excess of ammonium carbonate, heat and filter. This will remove all bases except K, and Na. The filtrate must now be evaporated to dryness, and ignited to expel  $\text{NH}_3$  salts. If a white saline residue

is left, the presence of K, of Na, or of both, is proved. Dissolve residue in a little water, acidify with HCl and add excess of solution of  $\text{PtCl}_4$ , and a little alcohol, if a yellow crystalline pp. is produced, K is present. Now add  $\text{NH}_4\text{Cl}$  in excess, allow to stand for a short time, filter, evaporate filtrate to dryness and ignite. If a white saline residue remains Na is present. Confirm by moistening residue with alcohol and inflaming, noting the yellow colour of the flame.

## PART II.

### *Detection of the Acids*

In examining the original solution with a view of detecting the particular acids which may be present, the acids, if any, which have been used in effecting the solution of the substance, should be remembered. It should also be noted that the presence of the following acids will probably have been revealed during the course of the preliminary examination and the search for bases, viz., carbonic, hydrosulphuric, hyposulphurous, chromic, arsenic, phosphoric, arsenious and silicic. while nitric and chloric acids will also (if present) have been most likely detected. With a knowledge of the bases that have been discovered, the particular acids which are likely to accompany them may be inferred with more or less accuracy.

The following mode of examination may be adopted :—Acidify a portion of original solution with HCl, and add  $\text{AgNO}_3$  in excess ; a white pp. indicates HCl, HBr ; a yellowish white pp. shows HI ; a dark red pp. indicates  $\text{CrO}_3$  ; add a moderate excess of  $\text{NH}_3$ , and filter quickly, if the filtrate, on the addition of excess of  $\text{HNO}_3$ , yields a white curdy pp., HCl is present. The following are the special tests for the different acids which may be applied to fresh portions of the original solution :—

NAME OF ACID	SPECIAL TEST
SULPHURIC	{ Acidify with HCl, and add BaCl <sub>2</sub> ; a white finely divided pp. indicates H <sub>2</sub> SO <sub>4</sub> .
NITRIC	
	{ Add H <sub>2</sub> SO <sub>4</sub> and some copper turnings and heat, the evolutions of ruddy acid fumes indicates HNO <sub>3</sub> , or HNO <sub>2</sub> .
PHOSPHORIC	{ If only alkalis are present, acidify with acetic acid, and add uranium acetate; a pale yellow pp. indicates H <sub>3</sub> PO <sub>4</sub> . If other metals are present, remove with excess of ammonium sulphide and NH <sub>3</sub> , filter, boil filtrate with excess of acetic acid until all odour of H <sub>2</sub> S has disappeared, again filter and apply test to filtrate. The following test may also be applied. Acidify with HCl, add a few drops, Fe <sub>2</sub> Cl <sub>3</sub> , then sodium acetate in excess. Light brown gelatinous pp. indicates H <sub>3</sub> PO <sub>4</sub> .
HYPOSULPHUROUS	
	{ Add H <sub>2</sub> SO <sub>4</sub> , and heat gently, a white pp. of sulphur, and an evolution of SO <sub>2</sub> indicates the presence of the acid.
BORACIC	{ Remove Cu (if present) by H <sub>2</sub> S, evaporate solution, mix with alcohol and inflame; a green flame shows the presence of the acid.
HYDROBROMIC	{ Add chlorine water, then shake with ether, if, on standing, the ether rises to the top, coloured deep brown, HBr is present, or HI is present.
HYDRIODIC	

To distinguish the two acids, test a fresh portion of original solution by adding potassium nitrite, HCl, and finally starch paste; a blue coloration indicates HI:—

CHROMIC	{ Acidify solution with acetic acid. It will now give with AgNO <sub>3</sub> a dark red pp., and with lead acetate a yellow pp.
ARSENIOUS	
	{ Acidify with acetate acid, add, AgNO <sub>3</sub> yellow pp., indicates As <sub>2</sub> O <sub>3</sub> . Solution of CuSO <sub>4</sub> will give a pp. of Scheele's green.
ARSENIC	{ Acidify with nitric acid, red pp. with AgNO <sub>3</sub> . May be distinguished from the similar reaction with CrO <sub>3</sub> by the original solution not giving a yellow pp. with lead acetate.

## PART II.



# ORGANIC CHEMISTRY

## INTRODUCTION

THE division of the Science of Chemistry into "organic" and "inorganic," was made at a time when it was believed that the so-called organic substances could only be produced by the agency of vital force in the living organs of plants and animals. At the present time, however, the barrier line between organic and inorganic chemistry has disappeared, as substances originally supposed to be produced solely under the influence of animal or vegetable life have been artificially prepared in the laboratory. At the same time it must be remembered, that although some of the regular and definite compounds produced under the influence of vitality have been prepared artificially, that there has as yet been no artificial production of such a distinctly *organised* product as cell structure. *Organised structures* are peculiar to life and growth, and are never found apart from these agencies. The term "organic chemistry" is now used to define that portion of chemical science which treats of the carbon compounds, these substances being so numerous and complicated, that it is most convenient to consider their production and properties under a distinct heading. Organic compounds not only include those which are found to exist in the various structures of animal and vegetable life, these which may be termed *natural products*, but also many others which have been built up—it might almost be said—created, in the laboratory of the chemist. The number of the so-called carbon compounds considerably exceeds the total number of the compounds of all the other elements, and additions to the list are being continually made by fresh discoveries. By far the greater number of known carbon compounds are formed by the union of carbon with one or more of the three other elements, hydrogen, nitrogen, and oxygen, while a *lesser number* contain also such elements as sulphur,

## CHAPTER I.

### DETERMINATION OF COMPOSITION OF CARBO

A KNOWLEDGE of the methods employed in the analysis of the carbon compounds is a necessary step in organic chemistry, for it is by this means that the composition is determined. The method of analysis is dependent on the nature of the compound to be determined, and the subject will be divided into distinct headings.

#### *Analysis of Compounds containing only Hydrogen, and Oxygen*

When any compound of carbon and hydrogen is heated to redness in contact with excess of oxygen, a true combustion is effected, in which the carbon becomes carbonic acid, and the hydrogen, water. If a known weight of the substance be taken, and the combustion products collected separately, the composition of the compound under examination can be readily calculated.

This combustion may be effected in a current of pure oxygen, but is more generally performed by means of pure cupric oxide, which at a red heat readily parts with its oxygen to organic substances. In making the analysis a tube of hard Bohemian glass (termed a combustion tube) is taken, and one end is drawn out to a fine point and sealed. The tube is then filled to about one-quarter of its entire length with granulated and recently ignited cupric oxide. About 0.3 to 0.5 gramme of the substance to be examined, which should be in fine powder, is then introduced into the tube, and rinsed down and mixed with fresh cupric oxide. The greatest care must be taken that the whole of the weighed quantity of material is thus brought into the tube, which is then filled to within two inches of the open end with a further quantity of cupric oxide. The combustion tube is then placed in a specially constructed furnace, furnished with a row of small Bunsen burners, each of which is provided with a tap, so that the heat may be regulated as desired (see fig. 7), and the tube is then connected by means of a well-fitting dry cork with the apparatus for collecting the combustion products. First, there is a tube charged with dry porous fragments of calcium chloride, to absorb and retain the water produced by the oxidation of the hydrogen of the organic compound. To this is connected, by a short length of caoutchouc tubing, a bulb apparatus, charged with caustic potash solution, which absorbs the carbonic acid produced during the combustion. The potash bulb apparatus has a further tube, containing dry calcium chloride, in order to retain any aqueous vapour which may be carried forward from the potash solution. The weight of the first drying tube, and that of the potash bulb apparatus, with its attached chloride of calcium tube, is carefully ascertained before commencing an experiment. Everything being ready, and all the connections thoroughly sound, the front part of the *combustion tube*, containing cupric oxide only, is heated



to redness by lighting the gas burners immediately under that part, and the heat is gradually brought, by lighting successive burners, to that portion of the tube containing the admixture of cupric oxide and the organic substance, the application of heat being so regulated that the bubbles of gas only slowly enter the potash bulbs. When gas has ceased to be evolved, the whole length of the tube is strongly heated for a few minutes, the fine end of the combustion tube is broken off, and a little air drawn through the apparatus, by applying a gentle suction to the extremity of the drying tube attached to the potash bulbs. This proceeding is necessary in order to bring the last traces of aqueous vapour and carbonic acid from the combustion tube into the absorption tubes. The latter are now disconnected and carefully weighed, when the amount to which the drying tube has increased in weight gives the amount of water, while the increase in the weight of the potash bulb and its attached drying tube, gives the amount of carbonic acid. Throughout the operation the greatest care must be taken, and the most minute attention given to manipulative details. When the substance is a volatile liquid, a slight variation in the method of treatment has to be adopted. In this case a small glass bulb furnished with a fine tube is carefully weighed, a small quantity of the liquid introduced, the point of the tube sealed, and the weight again ascertained, when the increase in weight gives the amount of liquid taken. The point of the tube is then broken, and the bulb dropped into the combustion tube. In the case of fatty or fixed oily bodies, the weighed quantity is placed in a small porcelain or platinum boat, which is pushed into the combustion tube. In each case the alternation of copper oxide, the substance to be examined, followed by fresh oxide, is preserved as already described.

If oxygen is present in the substance, besides carbon and hydrogen, its amount is estimated by the difference

between the weight of the substance taken, and the amounts of its other constituents.

### *Analysis of Organic Substances containing Nitrogen*

In cases where a compound contains nitrogen in addition to carbon and hydrogen, a modification of the process of analysis has to be adopted. When an organic nitrogen compound is heated with cupric oxide, part of the nitrogen is liberated in the free state, and part as nitric oxide. The latter substance is absorbed by the potash solution, and would thus give an error in the carbon determination. In order to obviate this, a roll of clean metallic copper is placed in the fore part of the tube, immediately in front of the cupric oxide, any nitric oxide is then decomposed by the metallic copper, nitrogen alone passing on, which does not affect the accuracy of the analysis. In order to *determine the amount* of nitrogen present, a weighed quantity of the material is intimately mixed with soda lime (a mixture of sodic hydrate and calcic oxide), and heated in a combustion tube, in which the nitrogen is liberated in the form of ammonia. The ammonia is absorbed by passing the gases evolved during the operation into a bulb tube containing dilute hydrochloric acid, ammonium chloride being formed. The ammonia is then estimated by adding platinic chloride to the solution, and collecting and weighing the double chloride of platinum and ammonium which is precipitated. Some bodies do not, however, yield the whole of their nitrogen in the form of ammonia by heating with soda lime, and in these cases, the nitrogen is estimated by heating the compound with cupric oxide and metallic copper, when the whole of the nitrogen is evolved in the free state, and after passing through soda solution to absorb *carbonic acid*, is estimated by careful measurement.

*Estimation of Sulphur, Chlorine, Bromine, Iodine, and Phosphorus, in Organic Bodies*

If any of these elements are present in an organic substance, the carbon and hydrogen determinations have to be effected by means of lead chromate in place of cupric oxide, for when the latter is employed, volatile compounds, such as sulphurous acid, copper chloride, or bromide, etc., are formed, which interfere with the accuracy of the determination. By the use of lead chromate non-volatile lead compounds are formed (sulphate, bromide, etc.), which remain behind in the combustion tube. Chlorine, bromine, and iodine, are generally estimated by exposing a mixture of the substance with pure lime to a red heat in a tube, when calcium chloride, bromide, or iodide is formed. The contents of the tube are then dissolved in nitric acid, and the precipitation effected by the addition of silver nitrate, the precipitate being collected and weighed.

Sulphur and phosphorus are determined by fusing the organic compound with a mixture of potassium nitrate and sodium carbonate, when sulphuric and phosphoric acids are produced, which are estimated by any of the well-known methods.

*Calculation of Results*

It will not be here necessary to give the mode of calculating the composition of a complex organic substance, containing, in addition to carbon, hydrogen, and oxygen, such elements as nitrogen, sulphur, or chlorine. It will suffice to give as an illustration, the analysis of a comparatively simple carbon compound, containing carbon, hydrogen, and oxygen, such, for instance, as acetic acid. Let us assume that 0.432 gram of this substance has yielded .633 gram of carbonic anhydride, and .259 gram of water. These quantities are re-

pectively equal to  $\cdot 1726$  gram of carbon, and  $\cdot 0288$  gram of hydrogen, from which the composition of 100 grams of the material is calculated, giving:—

Carbon	.	.	.	.	39.95
Hydrogen	.	.	.	.	6.66
Oxygen (by difference)	.	.	.	.	53.39
					<hr/>
					100.00

### *Calculation of Formula from Percentage Composition*

The analysis of an organic substance gives, as already shown, the composition per cent. From the figures thus obtained the relative equivalent proportions of the individual elements is obtained by dividing each number by the atomic weight of the substance. Thus, taking the analysis given, the carbon came to 39.95 per cent., which, divided by 12, gives 3.33; the hydrogen to 6.66, which, divided by 1, gives 6.66; and the oxygen to 53.39, which, divided by 16, gives 3.33. These numbers are in the proportion of 1 : 2 : 1, and the simplest possible formula to be assigned is  $\text{CH}_2\text{O}$ . The molecule may, however, contain, in place of  $\text{CH}_2\text{O}$ , some multiple of these numbers, and this point is of the greatest importance. In order to ascertain the *molecular* formula of the compound, there are two methods used, both of which are sometimes applicable, and occasionally but one, according to the nature of the substance. One method for the determination of the vapour density is adopted in the case of compounds which are capable of being converted into vapour at moderate temperatures; the other method is by forming some compound of the substance to be examined with some well-known element, and by a careful analysis of the compound, to ascertain the number of the *respective atoms present*.

*Determination of Vapour Density*

The simplest method of ascertaining the vapour density of a substance is that known as *Dumas'*, and which is carried out as follows:—A light globular flask, with its neck drawn out to a fine point, is taken, and the weight carefully ascertained, the atmospheric temperature and the height of the barometer being noted. A quantity of the substance to be examined is then introduced, and the flask is plunged into a bath of water, oil, or fusible metal, the temperature of which considerably exceeds the boiling point of the substance, which, under these conditions, is rapidly converted into vapour, making its escape from the neck of the flask. When the issue of vapour has ceased, from the complete volatilisation of the material, the neck of the flask is sealed by directing the flame of the blow-pipe on to its extremity, and, at the same time, the temperature of the bath is noted, and also the height of the barometer. After being allowed to cool, the outside of the flask is wiped, and its weight carefully ascertained. The extremity of the neck of the flask is now broken off under mercury, when the liquid rushes in and completely fills the vessel, if the experiment has been successful. From the volume of mercury thus entering, the capacity of the flask is ascertained. All the necessary data have now been obtained, and, as an example, it will be assumed that glacial acetic acid is the subject of the experiment, and, for the sake of simplicity, that the temperature and pressure of the air remained constant during the experiment; the thermometer being  $16^{\circ}$ , and the barometer standing at 756 millimetres. It will also be assumed that at the time of sealing the neck of the flask the temperature of the bath was  $280^{\circ}$ .

The weights obtained were as follow:—

Weight of flask filled with dry air

at  $16^{\circ}$  and 756 m.m. . . . . = 25.489 grama

Weight of flask filled with vapour

at 280° and 756 m.m. . . = 25·508 grams

Capacity of flask, 184 C.C.

We have first to ascertain what is the weight of 184 C.C. of dry air, at a temperature of 16° and pressure of 756 m.m. Now, 184 C.C. of air at 16° and 756 m.m. would become, at 0° and 760 m.m., reduced to 172·9 C.C. 1000 C.C. of air at 0° and 760 m.m. weigh 1·293 grams, and the weight of 172·9 C.C. will be, therefore, ·2235 grams. By deducting this quantity from the original weight of the flask in air, we get  $25·489 - ·2235 = 25·2665$ , the weight of the empty flask. By deducting the weight of the empty flask from that of the flask filled with vapour, we get  $25·508 - 25·2665 = ·2425$ , the weight of the vapour.

The weight, therefore, of 184 C.C. of the vapour of the substance, at 280° and 756 m.m., is ·2425 grams. As all gaseous densities are referred to hydrogen as the unit, we have now to find what is the weight of an equal volume of hydrogen at the same temperature and pressure. 184 C.C., at 280° and 756 m.m., would become reduced to 90·3 C.C. at 0° and 760 m.m.; and as 1000 C.C. of H. at 0° and 760 m.m. weigh ·00807 grams, the weight of the 90·3 C.C. will be ·00807 grams. By now dividing the weight of the vapour by that of the hydrogen, we obtain the density  $\frac{·2425}{·00807} = 30·04$ .

As the density of a compound vapour is half its molecular weight, the molecular weight to be assigned to the substance is 60·08, which corresponds to the formula  $C_2H_4O_2$ , the molecular weight of which is 60·0. It will be remembered, that in the analysis of acetic acid, numbers were obtained which showed that the simplest formula which could be assigned was  $CH_2O$ ; but there was no evidence to show whether the molecule was  $CH_2O$ , or some multiple of these numbers. It will be seen that the vapour density

would be incompatible with the formula  $\text{CH}_2\text{O}$ , the molecular weight of which would be 30, and vapour density 15. As the density found by experiment was 30, giving a molecular weight of 60, the correct formula to be assigned to a molecule of acetic acid is twice  $\text{CH}_2\text{O}$ , or  $\text{C}_2\text{H}_4\text{O}_2$ .

A further method of ascertaining vapour density, is to heat a weighed quantity of the substance, in a graduated tube, over mercury to a temperature exceeding its boiling point, and to carefully measure the volume occupied by the vapour. For this method, a correct apparatus has been devised by Guy-Lussac and Hoffman.

*Calculation of the Molecular Weight of a Substance  
from an Examination of its Compounds*

This mode of ascertaining molecular weight is not only applied to corroborate the data obtained by the determination of vapour density, but is often applicable in cases where ascertaining vapour density is not possible, as for instance, where the substance to be examined decomposes under the influence of heat, or where it is not possible to command a sufficient degree of temperature to affect the determination. By uniting the substance to be examined with another substance or element, whose powers of combination are well known, it is easy to find the correct molecular weight of the substance under examination. As we have so far spoken of acetic acid as an illustration of organic analysis, and of determination of vapour density, we will here continue the illustration by speaking of the same substance. The element silver is a monad, that is, it replaces one atom of hydrogen in combination. Acetic acid forms with silver a well-defined crystalline compound, viz., silver acetate, which is found to contain 64.68 per cent. of silver, leaving 35.32 for the acetic

acid. The equivalent weight of silver is 108, and as 64.68 of silver are united to 35.32 of acetic acid, the equivalent of silver (108) would require 58.97 of the acid. One equivalent of hydrogen in the acetic acid has, however, been displaced by the monad silver in combination, which must be added to the 58.97, making 59.97, or 60.0, which is therefore the molecular weight of acetic acid corresponding to the formula  $C_2H_4O_2$ .

#### FRACTIONAL DISTILLATION AND BOILING POINT

In the examination of volatile organic liquids possessing different boiling points, fractional distillation is often resorted to, as a means of separation, and the boiling points are also of importance as a physical distinction of these various liquids, and as a test of their purity. In the homologous series, for instance, the boiling point is found to rise steadily with the increase of carbon. The determination of boiling point is made by allowing the vapour of the boiling liquid to pass over the bulb of a thermometer. Fractional distillation is effected, by placing the liquid in a flask, to the neck of which is fitted a tube expanding into a bulb, in which is placed a thermometer; to this bulb is connected a tube leading to a small glass Liebig's Condensor. A series of small flasks may be used to collect the products of distillation. When a mixture of liquids, having different boiling points, is placed in the flask, and heat applied, the most volatile liquid distils over first, the thermometer showing the boiling point; when the mercury in the thermometer rises, it is an indication that the whole of the most volatile liquid has passed over, and the receiver is changed, in order to collect the next in succession. By repeating this process several distillates are obtained, each of which consists of a distinct compound. In order, however, to obtain each substance in a state of purity, it is necessary to again subject each portion to a further *fractional* distillation, rejecting the first and last



portions. This precaution is necessary, from the fact, that when a mixture of liquids of various boiling points is distilled, each liquid which passes over has a tendency to carry with it small quantities of those other liquids, whose boiling points more or less approximate to its own.

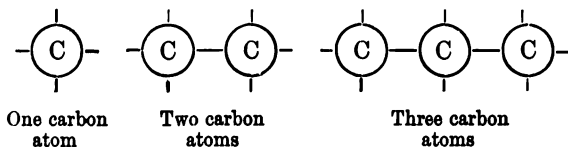
### *General Characteristics of the Carbon Compounds*

One of the most characteristic features of the carbon compounds is the large number of atoms often occurring to form a complete molecule. Thus, starch contains at least twenty-four constituent atoms, while in tri-stearin there are no less than 173. The peculiarity of carbon in forming such complex molecules is explained by assuming that the tetrad carbon atoms possess, to a greater degree than those of any other element, the property of uniting among themselves, at the same time that they combine with other elements. By this means partially saturated carbon radicals unite among themselves by a species of reduplication to form complex molecules containing a large number of constituent atoms; and other compounds, of even greater complexity of structure, are formed from the union of partially saturated radicles of different composition.

The simplest compound of the tetrad carbon is marsh gas,  $\text{CH}_4$ , containing one equivalent of carbon to four of monad hydrogen. This is, therefore, a fully saturated compound, in which the atomicity of the carbon is fully satisfied with the four equivalents of hydrogen. It is obvious that, as long as the atomicity of the carbon is satisfied, that a fully saturated compound is produced, and that any other monad element could take the place of hydrogen. Thus the compound  $\text{CCl}_4$  is known. A saturated carbon compound may also be produced, in which the four monad atoms are supplied by two elements, thus starting with marsh gas,  $\text{CH}_4$ , by the successive action of chlorine, the saturated compounds  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and

finally  $\text{CCl}_4$ , may be produced. When one element is thus substituted for another in a compound, the substance formed is termed a *substitution product*. The atomicity of carbon may also be satisfied, and fully saturated compounds formed, by two dyads, as in carbonic acid,  $\text{CO}_2$ , or by a triad and monad, as in hydrogen cyanide,  $\text{CHN}$ .

With carbon compounds containing a single equivalent of carbon it has been shown that there are four bonds of union to be satisfied; as, however, the complexity of the compounds increase, and a greater number of carbon atoms enter into the composition of the molecule, the active atomicity of the carbon is found to become less. This is assumed to arise from the fact that, in these complicated compounds, part of the bonds of attachment of the carbon atoms are engaged in satisfying each other. This will be better understood from the following graphic illustration, in which the carbon atom is shown with its four bonds of attachment.



It is thus seen that where two atoms of carbon are present in a compound, the active atomicity of the carbon is only six, and where three carbon atoms are joined, the active atomicity is eight. It will also be seen that for every additional atom of carbon, the atomicity is only increased by two. This is capable of experimental demonstration, and an extensive series of compounds are known, formed by continued additions of  $\text{CH}_2$ , and called the homologous series; thus there is  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ , types of the monocarbon, di-

carbon, and tricarbon series respectively, all being saturated compounds. Many substances exist, in which the atomicity of the carbon is not fully satisfied, and these are known as non-saturated compounds. They show a tendency to unite directly with other elements to the extent of their unsaturated atomicity, and so to form fully saturated compounds. Thus carbonic oxide, CO, has two bonds of attachment unsaturated, and will take up two equivalents of chlorine to form chloro-carbonic oxide,  $\text{COCl}_2$ . Olefiant gas,  $\text{C}_2\text{H}_4$ , is also a non-saturated compound, which will unite with two equivalents of chlorine to form ethylene chloride,  $\text{C}_2\text{H}_4\text{Cl}_2$ . Further reference will be made to saturated and non-saturated compounds, under the head of "Classification of Organic Compounds." A curious fact in connection with the carbon compounds is, that many of these compounds are found to have the same composition, and yet to differ in their physical and chemical properties. Several distinct differences are observable in bodies of this nature, for which special terms have been invented; thus the term "*polymeric*" is used in relation to bodies possessing the same percentage composition, but possessing different vapour densities. In this case, the molecular weight is different. The following compounds are polymeric:—

Aldehyde	.	.	.	$\text{C}_2\text{H}_4\text{O}$
Acraldehyde	.	.	.	$\text{C}_4\text{H}_8\text{O}_2$
Paraldehyde	.	.	.	$\text{C}_6\text{H}_{12}\text{O}_3$

And also the following members of the homologous series:—

Ethylene	.	.	.	$\text{C}_2\text{H}_4$
Propylene	.	.	.	$\text{C}_3\text{H}_6$
Butylene	.	.	.	$\text{C}_4\text{H}_8$
Amylene	.	.	.	$\text{C}_5\text{H}_{10}$

It is noticeable that in polymeric bodies the molecular weight is always some multiple of the numbers expressing the simplest ratio of the constituent elements.

Bodies having *the same percentage composition and the same vapour density, but which exhibit differences in physical and chemical character* are termed *meta-meric*: thus, allylic alcohol, propionic aldehyde and acetone all contain  $C_3H_6O$ , but they possess different physical and chemical characteristics, and the constitutional formulæ are written as follows:—

Allylic alcohol	$C_3H_5OH$
Propionic aldehyde	$C_2H_5COH$
Acetone	$CO(CH_3)_2$

Again, the following bodies possess the same percentage composition and vapour density, but possess different characteristics:—

Butyric Acid	$C_4H_7O$	} O
	H	
Ethyl Acetate	$C_2H_5$	} O
	$C_2H_3O$	
Methyl propionate	$CH_3$	} O
	$C_3H_5O$	
Propyl formate	$C_3H_7$	} O
	CHO	

All these bodies have an empirical formula of  $C_4H_8O_2$ . A further class of substances are known which have *the same percentage composition, the same vapour density which differ in physical properties, such as specific gravity and boiling point, but which exhibit a similar behaviour under the influence of reagents*—such bodies are called *isomeric*. Isomerism occurs in the so-called aromatic group and in the paraffin series. For instance, the volatile oils of turpentine, lemon, juniper, etc., all have the composition  $C_{10}H_{16}$ , and resemble each other closely in their chemical relations, being chiefly distinguished by their odour, and by their action on polarised light. The term isomerism is sometimes used in the wide sense of including all bodies having the same percentage composition, but possessing different chemical and physical properties. In this broadest sense isomerism includes *polymerism*, *metamerism*, and isomerism in the restricted sense.

### THE EMPIRICAL AND RATIONAL FORMULÆ OF ORGANIC COMPOUNDS

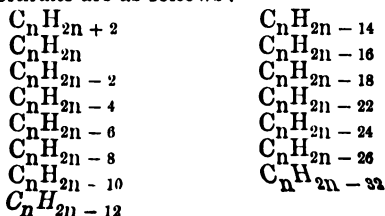
In mineral chemistry, where certain groups of elements can only represent one compound, the use of empirical formulæ cannot well give rise to any misapprehension as to the substance intended, but in organic chemistry, where so many bodies exist having the same percentage composition, and consequently the same empirical formulæ, it becomes, in most cases, absolutely necessary to adopt rational or constitutional formulæ. These formulæ are intended to convey some conception of the modes in which the compounds are formed, and in which they undergo decomposition. A compound may have several rational formulæ, according to the amount of information which it is intended to convey. Thus, acetic acid represented by the empirical formula,  $C_2H_4O_2$ , may be written  $H.C_2H_3O_2$ , if it is simply intended to convey the fact that the acid is monobasic, having one atom of replaceable hydrogen, which can be replaced by a single equivalent of a monad base—thus,  $NaC_2H_3O_2$ , and  $K.C_2H_3O_2$ , representing sodium and potassium acetates respectively. A formula conveying more knowledge of the *constitution* of acetic acid, is  $C_2H_3O.OH$ , having reference to the fact that when acted on by phosphorus pentachloride, the group (OH) is replaced by chlorine, forming  $C_2H_3OCl$ . A still more developed formula for acetic acid is  $CH_3CO(OH)$ , salts being formed by the substitution of base for the group (OH), thus—sodium acetate,  $CH_3CO(ONa)$ . Brackets are often useful in writing constitutional formulæ; by writing, for instance,  $CH_3CO(OH)$  with a bracket—thus,  $\left\{ \begin{array}{l} CH_3 \\ CO.OH \end{array} \right.$ , a better impression is conveyed as to the mode in which the elements are combined, the two carbon atoms joined, while the upper atom is satisfied by union with three atoms of hydrogen, and the lower carbon atom with oxygen, and with the monad group (OH).

Again, the empirical formula of ethane is  $C_2H_6$ , and

of ethyl alcohol,  $C_2H_6O$ . By writing ethane, however,  $C_2H_6$ , } and ethyl alcohol as  $C_2H_5$ , } O, the relation of the two compounds is better shown, the same radical,  $C_2H_5$ , being common to both.

### CLASSIFICATION OF ORGANIC COMPOUNDS

It has been already shown that the compound  $CH_4$  (Marsh Gas), is the simplest saturated hydrocarbon, and that a series of hydrocarbons are known, exhibiting a gradually ascending scale in which each member differs from the preceding one by  $CH_2$ . These hydrocarbons are known as *the homologous series*. In this series of *saturated* hydrocarbons, the starting point is the compound  $CH_4$ , and every additional atom of carbon is associated with two atoms of hydrogen; the general formula for the series is therefore  $C_nH_{2n+2}$ , and from such carbon compounds may be built up large families of organic substances. These compounds are frequently known as the monocarbon, dicarbon, and tricarbon series respectively, according to the number of carbon atoms present. From the series of *non-saturated* hydrocarbons, a further series of compounds are formed. They differ from the  $C_nH_{2n+2}$  series by even number of hydrogen atoms, and are obtained from the members of that series by the withdrawal of one or more pairs of hydrogen atoms. There are fifteen distinct series of hydrocarbon, the members of which have been obtained and investigated; the general formulæ are as follows:—



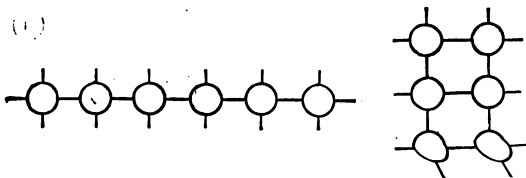
The following table gives the numbers of the series as far as  $C_6$ . In this table the first substance in the vertical columns is the starting point of the series, while the substances immediately beneath are its derived homologues:—

$CH_4$							
$C_2H_6$	$C_2H_4$	$C_2H_2$					
$C_3H_8$	$C_3H_6$	$C_3H_4$	$C_3H_2$				
$C_4H_{10}$	$C_4H_8$	$C_4H_6$	$C_4H_4$	$C_4H_2$			
$C_5H_{12}$	$C_5H_{10}$	$C_5H_8$	$C_5H_6$	$C_5H_4$	$C_5H_2$		
$C_6H_{14}$	$C_6H_{12}$	$C_6H_{10}$	$C_6H_8$	$C_6H_6$	$C_6H_4$	$C_6H_2$	

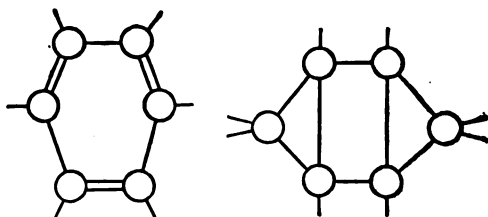
In this table it will be seen that in the vertical lines each member differs from the preceding by an addition of  $CH_2$ , and the series are consequently *homologous*, while each member in the horizontal line differs from the other by  $H_2$ , and forms what is termed an *isologous* series.

All the compounds of organic chemistry may be regarded as being formed more or less directly from the isologous series and their homologues, each member of each series forming a starting point for the formation of a number of compounds, all containing a common constituent, and exhibiting a family likeness. In the homologues of marsh gas or methane, for instance, we may assume the existence of compound radicals which impart a characteristic to the members of each group. Thus, marsh gas,  $CH_4$ , may be regarded as a compound of hydrogen with a radical called methyl, and regarded as methyl hydride,  $\left. \begin{smallmatrix} CH_3 \\ H \end{smallmatrix} \right\}$ . In the same way the next member of the series,  $C_2H_6$ , may be regarded as ethyl hydride,  $\left. \begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \right\}$  and the next member, again  $C_3H_8$ , as propyl hydride,  $\left. \begin{smallmatrix} C_3H_7 \\ H \end{smallmatrix} \right\}$ . By replacing the hydrogen by chlorine we obtain the corresponding chlorides,  $\left. \begin{smallmatrix} CH_3 \\ Cl \end{smallmatrix} \right\}$ ,  $\left. \begin{smallmatrix} C_2H_5 \\ Cl \end{smallmatrix} \right\}$  and  $\left. \begin{smallmatrix} C_3H_7 \\ Cl \end{smallmatrix} \right\}$  while

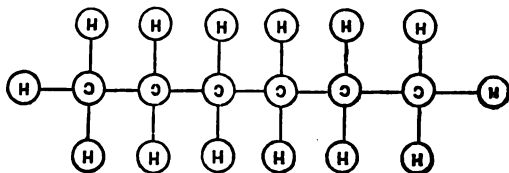
by replacing the hydrogen by the monad radical hydroxyl the *alcohols* are obtained,  $\begin{smallmatrix} \text{CH}_3 \\ \text{HO} \end{smallmatrix} \}$  or  $\begin{smallmatrix} \text{CH}_3 \\ \text{H} \end{smallmatrix} \} \text{O}$ ,  $\begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \} \text{O}$ , and  $\begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{H} \end{smallmatrix} \} \text{O}$ . It will be observed that the respective radicals,  $\text{CH}_3$  methyl,  $\text{C}_2\text{H}_5$  ethyl, and  $\text{C}_3\text{H}_7$  propyl, are present throughout the corresponding compounds, and the same view may be taken of the higher members of the series. The radicals in organic chemistry, like those in inorganic chemistry, have distinct atomicities, and are monads, dyads, triads or tetrads. All those in which the atomicity is greater than one, are called polyatomic radicals. The hydrocarbons of the series,  $\text{C}_n\text{H}_{2n+2}$ , and their derivatives, are sometimes spoken of as "the Paraffin series," while those containing not less than six carbon atoms, so arranged as to leave only six combining units unsaturated, are termed "the aromatic group." In non-saturated compounds it must be remembered that the number of carbon bonds saturated by union with each other, and the number of bonds left open for further combination, depends on the arrangement of the atoms in the molecule. For instance, groups of carbon atoms may be *assumed*, in which by different arrangements a variable (but even) number of bonds of attachment may remain unsaturated. The following sketches exhibit some of these hypothetical arrangements of a six carbon group:—



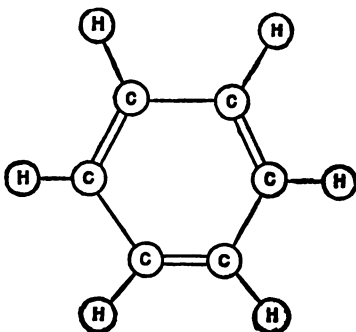




In which by different arrangements the active atomicity is 14, 10, 6, and 8 respectively. Taking two members of different series, each containing six carbon atoms, it will be seen at once how the arrangement of carbon atoms in the molecule affects the number of bonds of attachment in union with other elements. Thus, Sextine,  $C_6H_{14}$ , one of the Paraffin series, a homologue of methane or marsh gas, is a saturated hydrocarbon containing fourteen bonds of attachment united to hydrogen, while benzene,  $C_6H_6$ , belonging to the so-called aromatic series, is also a saturated compound in which only six bonds are united to hydrogen. The mode of union in each case is illustrated by the following graphic representation :—



Sextine



Benzine

In preference to adopting the classification of organic bodies into the Paraffin series and the aromatic series, we shall adopt a more extended classification, but one which indicates more clearly and more definitely the relation between groups of compounds possessing many leading characteristics in common, the members of each group being prepared by very similar means. The following indicates the arrangement in which the various organic compounds will be studied :—

1. HYDROCARBONS AND THEIR HALOID DERIVATIVES.

—This group includes the hydrocarbons, the general formulæ of which have been given, together with their so-called haloid derivatives—that is, compounds obtained from the hydrocarbons by the action of chlorine, bromine, or iodine.

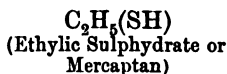
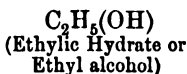
The following may be taken as examples :—

HYDROCARBON	HALOID DERIVATIVES
Methane, $\text{CH}_4$	$\text{CH}_3\text{Cl}$ , $\text{CH}_2\text{Cl}_2$ , $\text{CHCl}_3$ , $\text{CCl}_4$ , $\text{CH}_3\text{I}$ , etc.
Ethane, $\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_5\text{Cl}$ , $\text{C}_2\text{H}_4\text{Cl}_2$ , $\text{C}_2\text{H}_3\text{Cl}_3$ , &c.

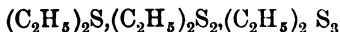
All such haloid derivatives are formed by the substitution of the respective haloids for hydrogen. The

group also includes bodies in which such monatomic groups, as (CN), (SCN), (NO<sub>2</sub>), or (NH<sub>2</sub>), replace corresponding hydrogen atoms.

2. ALCOHOLS.—The alcohols may be assumed as hydrocarbons in which one or more atoms of hydrogen are replaced by monad hydroxyl (OH). This group also includes bodies termed thio-alcohols or mercaptans, in which the group (SH) takes the place of hydrogen, thus—



3. ETHERS.—The Ethers may be regarded as the anhydrides of the alcohols: thus, ethylic oxide or ethyl is (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, while methylic oxide or methyl ether is (CH<sub>3</sub>)<sub>2</sub>O. This group also includes bodies of analogous composition containing sulphur, thus—



4. ALDEHYDES.—These are bodies standing in an intermediate position between alcohols, and the corresponding acids. They are formed by the oxidation of the corresponding alcohols, from which they differ in containing two atoms less of hydrogen, thus—

(1) Methyl Alcohol, CH<sub>3</sub>OH, yields CH<sub>2</sub>O or H.CO.H,  
Formic or Methylic Aldehyde

(2) Ethyl Alcohol, C<sub>2</sub>H<sub>5</sub>OH, yields C<sub>2</sub>H<sub>4</sub>O or CHC<sub>2</sub>OH,  
Acetic or Ethylic Aldehyde

5. KETONES.—These compounds may be regarded as derived from aldehydes by the replacement of the hydrogen atom in the group (COH) by monatomic hydrocarbon groups — thus, ordinary acet-aldehyde, CH<sub>3</sub>.COH becomes CH<sub>3</sub>.CO.CH<sub>3</sub>.

6. ACIDS.—These substances may be regarded as compounds of oxygenated radicals, with hydroxyl, or as derived from hydrocarbons by the substitution of the monad group, CO.OH (carboxyl), for hydrogen;

thus, acetic acid may be written  $C_2H_3O.HO$ , or  $CH_3CO(OH)$  derived from ethyl,  $C_2H_5$ . It is observable that the organic acids contain two atoms less hydrogen than the hydrocarbons from which they are derived, and contain in addition two atoms of oxygen.

The organic acids give rise to a large class of derivatives, including metallic salts, haloid salts, ethereal salts, acid chlorides, bromides, and iodides, amides, and haloid derivatives.

7. ANHYDRIDES.—These compounds bear the same relation to the acids that the ethers have to the alcohols, thus—

Ethyl alcohol,  $C_2H_5OH$ . Ethyl ether,  $\left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\} O$ .

Acetic acid,  $CH_3CO.OH$ . Acetic anhydride  $\left. \begin{matrix} CH_3CO \\ CH_3CO \end{matrix} \right\} O$ .

8. AMINES.—The amines, or organic ammonias, as they are sometimes called, are generally regarded as ammonia, in which hydrocarbon groups are substituted for hydrogen, thus—

Ethylamine,  $N \left\{ \begin{matrix} C_2H_5 \\ H \\ H \end{matrix} \right.$  Di-ethylamine,  $N \left\{ \begin{matrix} C_2H_5 \\ C_2H_5 \\ H \end{matrix} \right.$

Tri-ethylamine,  $N \left\{ \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} \right.$

9. ORGANO-METALLIC COMPOUNDS.—These substances may be regarded as compounds of the metals with monatomic hydrocarbon groups, thus—

Mercuric methide,  $Hg (CH_3)_2$ .  
Mercuric ethide,  $Hg (C_2H_5)_2$ .

The relations of the various classes into which the compounds of organic chemistry are divided is illustrated in the following table, in which is shewn a few selected hydrocarbons, in connection with the compounds derived from them.

*Table showing the relation of some of the Princip*

HYDROCARBON	ALCOHOL	ETHER
$\left. \begin{array}{l} \text{Methane or} \\ \text{Methyl, CH}_4 \end{array} \right\} = \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array} \}$	$\left. \begin{array}{l} \text{Methyl alcohol} \\ \text{CH}_3\text{OH, or } \begin{array}{c} \text{CH}_3 \\ \text{OH} \end{array} \end{array} \right\}$	$\left. \begin{array}{l} \text{Dimethyl ether} \\ (\text{CH}_3)_2\text{O, or } \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \end{array} \right\}$
$\left. \begin{array}{l} \text{Ethane or} \\ \text{Ethyl, C}_2\text{H}_6 \end{array} \right\} = \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \}$	$\left. \begin{array}{l} \text{Ethyl alcohol} \\ \text{C}_2\text{H}_5\text{OH, or } \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{OH} \end{array} \end{array} \right\}$	$\left. \begin{array}{l} \text{Diethyl ether} \\ (\text{C}_2\text{H}_5)_2\text{O, or } \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \end{array} \right\}$
$\left. \begin{array}{l} \text{Propane or} \\ \text{Propyl, C}_3\text{H}_8 \end{array} \right\} = \begin{array}{c} \text{C}_3\text{H}_7 \\ \text{H} \end{array} \}$	$\left. \begin{array}{l} \text{Propyl alcohol} \\ \text{C}_3\text{H}_7\text{OH, or } \begin{array}{c} \text{C}_3\text{H}_7 \\ \text{OH} \end{array} \end{array} \right\}$	$\left. \begin{array}{l} \text{Dipropyl ether} \\ (\text{C}_3\text{H}_7)_2\text{O, or } \begin{array}{c} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{array} \end{array} \right\}$
$\left. \begin{array}{l} \text{Tetane or} \\ \text{Butyl, C}_4\text{H}_{10} \end{array} \right\} = \begin{array}{c} \text{C}_4\text{H}_9 \\ \text{H} \end{array} \}$	$\left. \begin{array}{l} \text{Butyl alcohol} \\ \text{C}_4\text{H}_9\text{OH, or } \begin{array}{c} \text{C}_4\text{H}_9 \\ \text{OH} \end{array} \end{array} \right\}$	$\left. \begin{array}{l} \text{Dibutyl ether} \\ (\text{C}_4\text{H}_9)_2\text{O, or } \begin{array}{c} \text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 \end{array} \end{array} \right\}$
$\left. \begin{array}{l} \text{Quintane} \\ \text{Pentane or} \\ \text{Amyl, C}_5\text{H}_{12} \end{array} \right\} = \begin{array}{c} \text{C}_5\text{H}_{11} \\ \text{H} \end{array} \}$	$\left. \begin{array}{l} \text{Amyl alcohol} \\ \text{C}_5\text{H}_{11}\text{OH, or } \begin{array}{c} \text{C}_5\text{H}_{11} \\ \text{OH} \end{array} \end{array} \right\}$	$\left. \begin{array}{l} \text{Diamyl ether} \\ (\text{C}_5\text{H}_{11})_2\text{O or } \begin{array}{c} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{array} \end{array} \right\}$

A few remarks on the above table will probably assist to a clearer comprehension of the relation between the different hydrocarbons and their derivatives. Starting with the hydrocarbon, it may be assumed to consist of a hydrocarbon radical united to one atom of hydrogen. This is not really the case, but is simply assumed to facilitate explanation. The formula of the corresponding alcohol is thus obtained by substituting OH for H. The ether contains two of the hydrocarbon radical groups, and one equivalent of oxygen. The ketone contains two of the hydrocarbon radical groups, united to the group (CO). The aldehyde contains two atoms of hydrogen less than the original

*Hydrocarbons to the Chief Compounds derived from them :—*

KETONE	ALDEHYDE	ACID
Dimethyl Ketone (Acetone) CO { $\text{CH}_3$ $\text{CH}_3$	Methylic or Formic Aldehyde $\text{CH}_2\text{O}$ , or $\text{HCOH}$	Methylic or Formic Acid $\text{CH}_2\text{O}_2$ , or $\text{HCO}(\text{OH})$
Diethyl Ketone (Propione) CO { $\text{C}_2\text{H}_5$ $\text{C}_2\text{H}_5$	Ethylic or Acetic Aldehyde $\text{C}_2\text{H}_4\text{O}$ , or $\text{CH}_3\text{COH}$	Ethylic or Acetic Acid $\text{C}_2\text{H}_4\text{O}_2$ , or $\text{CH}_3\text{CO}(\text{OH})$
Dipropyl Ketone (Butyrene) CO { $\text{C}_3\text{H}_7$ $\text{C}_3\text{H}_7$	Propylic or Propionic Aldehyde $\text{C}_3\text{H}_6\text{O}$ , or $\text{C}_3\text{H}_7\text{COH}$	Propylic or Propionic Acid $\text{C}_3\text{H}_6\text{O}_2$ , or $\text{C}_3\text{H}_7\text{CO}(\text{OH})$
Dibutyl Ketone (Valerone) CO { $\text{C}_4\text{H}_9$ $\text{C}_4\text{H}_9$	Tetrylic or Butyric Aldehyde $\text{C}_4\text{H}_8\text{O}$ , or $\text{C}_4\text{H}_9\text{COH}$	Tetrylic or Butyric Acid $\text{C}_4\text{H}_8\text{O}_2$ , or $\text{C}_4\text{H}_9\text{CO}(\text{OH})$
Diamyl Ketone (Caprone) CO { $\text{C}_5\text{H}_{11}$ $\text{C}_5\text{H}_{11}$	Pentylic or Valeric Aldehyde $\text{C}_5\text{H}_{10}\text{O}$ , or $\text{C}_5\text{H}_{11}\text{COH}$	Pentylic or Valeric Acid $\text{C}_5\text{H}_{10}\text{O}_2$ , or $\text{C}_5\text{H}_{11}\text{CO}(\text{OH})$

hydrocarbon, and contains in addition *one* equivalent of oxygen, while the corresponding acid contains two equivalents of hydrogen less than the original hydrocarbon, with the addition of *two* equivalents of oxygen.

The state of organic chemistry is at present such that there are many compounds whose constitution is but little understood, and whose relation to the hydrocarbons has not been traced ; such compounds cannot therefore be included in the classification which has been given, and must be considered apart. This is the case with many compounds formed in the animal organism, with many vegetable oils and resins, and with many of the so-called vegito-alkaloids.

## THE SIMPLE COMPOUNDS OF CARBON, WITH OXYGEN, SULPHUR AND NITROGEN.

The true oxides of carbon, carbon monoxide, and carbon dioxide, have been already described in mineral chemistry (Carbon). Carbonic oxide, however, forms some compounds which may be described here. The carbonic oxide in these compounds is termed carbonyl, and acts as a dyad radical.

CARBONYL CHLORIDE,  $\text{CO.Cl}_2$ , is also called phosgene, carbonic oxy-chloride, and chloro-carbonic acid. It is prepared by exposing a mixture of chlorine and carbonic oxide to the action of direct sunlight. It is a colourless gas of suffocating odour, and which may be condensed by cold to a colourless liquid, boiling at  $8^\circ$ . It is immediately decomposed by water into carbon dioxide and hydrochloric acid,  $\text{CO.Cl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$ .

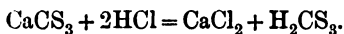
CARBONYL SULPHIDE,  $\text{CO.S}$ , is a colourless inflammable gas, obtained by passing carbonic oxide and the vapour of sulphur through a red-hot tube, or by acting on potassium sulphocyanide with dilute sulphuric acid.

## CARBON AND SULPHUR.

CARBON DISULPHIDE,  $\text{CS}_2$ .—This compound is not produced when carbon and sulphur are simply heated together, owing to the fact that the sulphur volatilises before the carbon is sufficiently heated to admit of combination. By passing the vapour of sulphur over carbon, previously heated to redness, combination ensues, and the carbon disulphide distils over and may be condensed. In the pure form, carbon disulphide is a mobile colourless liquid, possessing a peculiarly unpleasant odour. Its specific gravity is 1.26, and it boils at  $46^\circ$ , being very volatile and inflammable. It freely dissolves phosphorus, sulphur, iodine, oils, and

caoutchouc, and many resinous gums, and is largely employed for such purposes in the arts and manufactures. Carbon disulphide unites directly with the sulphides of the alkalis and alkaline earths to form salts called sulphocarbonates, thus— $\text{CS}_2 + \text{CaS} = \text{CaS} \cdot \text{CS}_2$ , or  $\text{CaCS}_3$ .

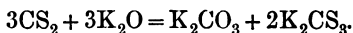
Sulphocarbonic acid is obtained by treating a sulphocarbonate with dilute hydrochloric acid.



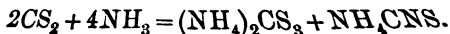
It is a yellow oily liquid, subject to spontaneous decomposition. By the action of carbon disulphide on a hot saturated solution of potash in alcohol, the potassium salt of xanthic acid is formed. On the cooling of the solution, potassium xanthate crystallises out in brilliant colourless prisms. From this salt the acid may be prepared by the action of dilute sulphuric or hydrochloric acid as a colourless oily liquid, which is combustible and heavier than water. Potassium xanthate has the composition  $(\text{C}_2\text{H}_5)_2\text{KCOS}_2$ , and is hence potassium ethyl-disulphocarbonate.

Xanthic acid forms a characteristic compound with copper. It is produced as a flocculent precipitate of a beautiful yellow colour by adding a soluble xanthate to a solution of a cupric salt.

Carbon disulphide, when heated with zinc and sulphuric acid, forms with the nascent hydrogen which is evolved a crystalline compound,  $\text{CH}_2\text{S}$ . The fixed caustic alkalis gradually dissolve carbon disulphide, forming a mixture of carbonate and sulphocarbonate, thus—



Aqueous solution of ammonia yields, with carbon disulphide, a mixture of sulphocyanide and sulphocarbonate—





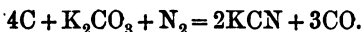
The compounds of carbon and *chlorine* will be noticed among the haloid derivative of the hydrocarbons.

CARBON AND NITROGEN. CYANOGEN,  $(CN)_2$ ,  
or  $C_2N_2$ .\*

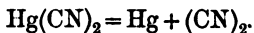
Cyanogen possesses a peculiar interest in being much allied to the halogens in its modes of action, and being thus, in a restricted sense, connected with inorganic chemistry, and in forming a large number of compounds more allied to substances generally classed as organic. Cyanogen is also a subject of great interest, from the fact that some of its compounds were among the first organic substances to receive a thorough investigation. The first cyanogen compound that attracted attention was Prussian blue, which was used as a colour for a considerable period before its composition was known or the rationale of its production understood. Some time afterwards, it was shown that Prussian blue could be produced by calcining dried animal refuse with potassium carbonate, and subsequent treatment of the solution obtained by the lixiviation of the fused mass with sulphate of iron and hydrochloric acid. Subsequently it was discovered by Macquer that the substance contained iron, which was afterwards confirmed by Scheele, who was the first to produce *Prussic* acid. The composition of Prussic acid was shown by Berthollet in 1787, and Porrett, in 1814, prepared ferrocyanic acid by decomposing Prussian blue with baryta, and afterwards removing the baryta by means of sulphuric acid. In 1815, Gay-Lussac obtained crystalline mercuric cyanide by boiling Prussian blue with red oxide of mercury and water, and by the action of heat on the mercury compound, cyanogen gas was first obtained, deriving its name from *κυάνεος*, blue, in allusion to its connection with Prussian blue.

\* In the cyanogen compounds, CN is often shortly written "Cy."

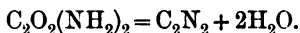
Carbon and nitrogen cannot be made to unite directly with each other, but by passing nitrogen over a mixture of charcoal and potassium carbonate at a white heat, a compound of cyanogen and potassium (potassium cyanide) is formed, thus—



From potassium cyanide may be formed a large number of substances containing the group (CN). On a large scale alkaline cyanogen compounds are prepared by heating any nitrogenous animal refuse with potassium carbonate. Cyanogen is generally obtained by the action of heat on the cyanides of mercury, gold, or silver, thus—



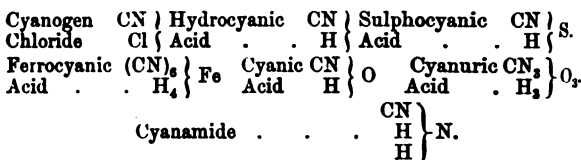
It may also be obtained by heating oxamide,  $\text{C}_2\text{O}_2(\text{NH}_3)_2$ , or ammonium oxalate,  $\text{C}_2\text{O}_4(\text{NH}_4)_2$ .



Cyanogen is a colourless gas which is extremely poisonous, and which possesses a peculiar odour of bitter almonds. It may be condensed to the liquid form by the application of cold or pressure, and at temperatures below  $-30^\circ$ , forms a white crystalline solid. Cyanogen is inflammable, and burns in the air with a violet flame, the products of combustion being carbonic anhydride and nitrogen. Cyanogen dissolves in water and in alcohol, but the solutions decompose spontaneously. Cyanogen exhibits close relations to the monad elements, chlorine, bromine, and iodine. When passed into a solution of potassium hydrate, a cyanide and a cyanate are formed simultaneously, the action thus exactly resembling that of chlorine—

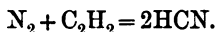


Cyanogen forms an extensive series of compounds, of which the following are some of the most important:—

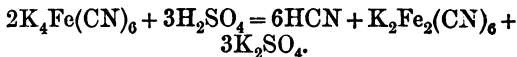


**CYANOGEN CHLORIDE, CNCl.**—By the action of chlorine upon hydrocyanic acid, the hydrogen is replaced by chlorine, thus— $\text{HCN} + \text{Cl}_2 = \text{HCl} + \text{CNCl}$ . Two polymeric modifications of cyanogen chloride are known; the one, CNCl, is liquid, and boils at 15.5, the other,  $(\text{CN})_3 \text{Cl}_3$ , is a solid, boiling at 190°.

**HYDROCYANIC ACID, HCN.**—This compound may be prepared synthetically by the passage of electric sparks through a mixture of acetylene and nitrogen.

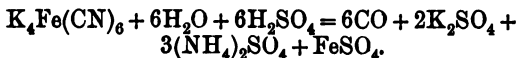


The anhydrous acid may be prepared by the action of perfectly dry hydrochloric acid gas or sulphurated hydrogen or mercuric cyanide.  $\text{Hg}(\text{CN})_2 + \text{H}_2\text{S} = 2\text{HCN} + \text{HgS}$ . It is a volatile liquid, which is a most violent poison. It is soluble in water and alcohol. Ordinary hydrocyanic acid as used in pharmacy is a dilute liquid prepared by distilling potassium ferrocyanide with dilute sulphuric acid.



For the sake of simplicity, the water used for diluting the acid is not shown to take part in the reaction, but as a matter of fact, it exercises a most important influence, for when sulphuric acid, with a very small quantity of water is used, the action is totally different,

the potassium ferrocyanide being entirely decomposed with formation of carbonic oxide, thus :—



Pure hydrocyanic acid is a very unstable substance, decomposing spontaneously, with formation of a brown amorphous product and ammonia. The dilute acid is also subject to a similar decomposition, but the presence of a trace of a mineral acid has a remarkable effect in increasing its stability. Hydrocyanic acid forms a series of *simple cyanides*, by action on metallic oxides, and a large number of *double cyanides* are also known. Of the simple cyanides, those of potassium and mercury are the most important. Potassium cyanide is formed when hydrocyanic acid is neutralised by a solution of potassium hydrate, and also by burning metallic potassium in cyanogen. On a large scale it is prepared by fusing a mixture of potassium ferrocyanide and potassium carbonate. The iron of the ferrocyanide is separated and replaced by potassium. Potassium cyanide is a white salt, which may be fused without decomposition. It is a violent poison. It is used largely in the arts for the electro-deposition of silver and gold, the double cyanides of which are soluble, and also in photography, for dissolving unaltered silver salts from the negative image. Sodium and ammonium cyanides are soluble and poisonous. Mercuric cyanide,  $\text{HgC}_2\text{N}_2$ , is a crystallisable soluble salt, prepared by dissolving mercuric oxide in ordinary hydrocyanic acid. Most of the other metallic cyanides are insoluble compounds; that of copper is brownish red, while the silver salt is white, and much resembles the chloride. Hydrocyanic acid may be quantitatively determined in solution, by acidifying with nitric acid and adding a solution of silver nitrate, when silver cyanide is precipitated, which is collected on a weighed

filter, washed, dried at  $100^{\circ}$ , and weighed; 134 parts of silver cyanide equal 27 parts of hydrocyanic acid.

**FERROCYANIDES.**—These are cyanogen compounds, containing iron as an element of their composition; the presence of the metal, cannot, however, be identified by any of the ordinary tests. The principal compound is the potassium salt,  $K_4Fe(CN)_6 + 3H_2O$ , and which is commonly known as yellow prussiate of potash. This salt is prepared on a large scale, by heating a mixture of nitrogenous organic matter with potash and iron filings. The fused mass is subsequently treated with water, and the clear solution yields an evaporation of pale yellow tetragonal pyramids of the salt, which does not possess poisonous properties. Potassium ferrocyanide is decomposed by exposure to a red heat, yielding potassium cyanide, nitrogen, and a compound of iron and carbon. The action of dilute and concentrated sulphuric acid on the salt has been already noticed. A solution of potassium ferrocyanide gives a white precipitate with a ferrous salt, and with ferric salts, a deep blue precipitate of Prussian blue, a ferrocyanide of iron and potassium,  $Fe_2K_22Fe(CN)_6$ . When acted on by a ferrous salt this compound is converted into ferric-ferrocyanide,  $Fe_22Fe(CN)_6$ . Commercial Prussian blue is a mixture of the two compounds, prepared by adding a mixture of a ferrous and ferric salt to a solution of potassium ferrocyanide. The ferrocyanides form insoluble compounds with many of the metals, one of the most characteristic being the copper salt,  $Cu_2Fe(CN)_6$ . Ferrocyanic acid, or hydrogen ferrocyanide,  $H_4Fe(CN)_6$ , may be prepared by acting on a strong solution of the potassium salt with hydrochloric acid. It is a strong acid, and is tetrabasic.

**FERRICYANIDES.**—The potassium compound of ferricyanic acid is produced by passing chlorine through a solution of prussiate of potash, until the solution ceases to give a blue precipitate with a ferric salt. The solu-

tion gives, on evaporation, red monoclinic crystals of  $K_3Fe(CN)_6$ . Ferricyanic acid is obtained by acting on the lead compound with sulphuric acid. It is very unstable. The ferricyanides of the alkalis are soluble, while those of the heavier metals are for the most part insoluble. A soluble ferricyanide gives no precipitate with ferric salts, but with ferrous salts yields a deep blue precipitate of  $Fe_32 Fe(CN)_6$ . This compound is slightly brighter in colour than ordinary Prussian blue, and is known as Turnbull's blue.

NITRO-FERROCYANIDES are produced by the action of nitric acid on soluble ferrocyanides. The sodium salt,  $Na_2Fe(CN)_5NO$ , is a well-defined compound, crystallizing in red prisms. The soluble nitro-ferrocyanides produce a beautiful purple colour, with the least trace of an alkaline sulphide.

SULPHOCYANIDES.—The potassium salt,  $KCNS$ , is formed by fusing a mixture of potassium ferrocyanide and sulphur. The salt crystallises in long white prisms, which are very deliquescent. Sulphocyanic acid,  $HCNS$ , may be obtained by acting on mercuric sulphocyanide with sulphurated hydrogen. The least trace of a soluble sulphocyanide may be identified by the production of a blood red colour with solution of ferric chloride. Mercuric sulphocyanide,  $Hg(CNS)_2$ , is a white insoluble powder, which is used for the preparation of "Pharaoh's serpents."

CYANATES.—A class of salts formed by the oxidation of cyanides. Potassium cyanide, by fusion with plumbic oxide or manganic peroxide, is converted into potassium cyanate. A cyanate is also formed, together with a cyanide, by the action of cyanogen on potash solution.

CYANIC ACID is produced by the distillation of a polymeric compound cyanuric acid. It must be condensed by the use of a freezing mixture, and then forms a colourless, strongly acid liquid of pungent odour, which rapidly changes to crystalline cyanamide. In

contact with water it forms ammonium then urea by reaction on the ammonia.



Cyanic acid is monobasic. The ammonium salt is formed by the direct union of dicyanogen and cyanic acid, but changes slowly at ordinary temperature and instantly at  $100^\circ$ , into urea.

CYANURIC ACID,  $\text{C}_3\text{H}_3\text{O}_3$ , is a polymer formed by the action of water on cyanogen chloride, and is also produced by heating cyanogen.

CYANURIDE is another polymer of cyanogen.

CYANAMIDE,  $\text{CN}(\text{H}_2\text{N})_2$ , is a white solid obtained by the action of gaseous cyanogen on ammonia.

DI-CYANAMIDE  $(\text{CN})_2\text{HN}$ , and *Tri-cyanamide* are also formed by the same means.

## HYDROCARBONS AND THEIR DERIVATIVES

$\text{C}_n\text{H}_{2n+2}$  or Marsh Gas Series.

The term Paraffin was first given to a substance obtained during the distillation of lignites, and also found in nature as ozokerit, but the word has been extended to a series of hydrocarbons, having the formula  $\text{C}_n\text{H}_{2n+2}$ . The word paraffin (from *paraffin*) denotes a peculiar chemical indifference to other bodies. A very large number of compounds are known, constituting a complete homologous series, of which the compound  $\text{CH}_4$ , called methane, is the first member. The following

## HYDROCARBONS AND THEIR HALOID DERIVATIVES 373

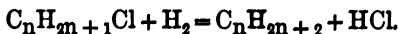
names and formulæ of the first ten members of the series :—

Boiling Point		Boiling Point	
{ Methane, CH <sub>4</sub> Ethane, C <sub>2</sub> H <sub>6</sub> Propane, C <sub>3</sub> H <sub>8</sub> Tetrane, C <sub>4</sub> H <sub>10</sub>	} Gaseous	Hexane, C <sub>6</sub> H <sub>14</sub>	70°
		Heptane, C <sub>7</sub> H <sub>16</sub>	99°
		Octane, C <sub>8</sub> H <sub>18</sub>	124°
		Nonane, C <sub>9</sub> H <sub>20</sub>	202°
Pentane, C <sub>5</sub> H <sub>12</sub>	38°	Decane, C <sub>10</sub> H <sub>22</sub>	278°

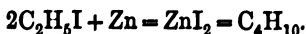
### MODES OF FORMATION

All the members of the group may be formed from the lowest, viz., methane, by successive addition of CH<sub>4</sub>, hydrogen being eliminated thus :—CH<sub>4</sub> + CH<sub>4</sub> = C<sub>2</sub>H<sub>6</sub> + H<sub>2</sub> C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub> = C<sub>3</sub>H<sub>8</sub> + H<sub>2</sub>.

The best method for the preparation of the various members of the series is by the action of nascent hydrogen on the monochlorinated or monoiodated paraffin, thus :—



By the action of metallic zinc on a haloid derivative of one member of the series, another of the series may be produced, thus :—



The best method of preparation in each case will be hereafter mentioned.

The various members of the paraffin series are often regarded as *hydrides* of radicals, thus methane, CH<sub>4</sub>, may be regarded as methyl hydride, CH<sub>3</sub>H, ethane as ethyl hydride, C<sub>2</sub>H<sub>5</sub>H, and so on. This view, although convenient, as showing, in an apparently simple way, the relation of each member of the series to some of its leading compounds, infers that the portion of hydrogen in union with the assumed radical has a different value to the other hydrogen atoms, a view *which has not yet been established*. Several of the



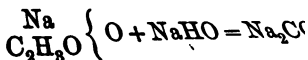
paraffin series form isomeric modifications. Methane, ethane, and propane, have not at present been found to have isomers, but two isomeric modifications of pentane are known, and each member of the series yields isomers.

The known paraffins may be classed into two series, of which the first series are the homologous series, methane, ethane, propane, etc., which are the normal paraffins, and can be converted directly into corresponding normal alcohols. The boiling points of the homologous members of the series increase with the ascending members of the series. It is observable that the normal paraffin is in each case the most stable than its isomers. The remaining paraffins are made up of isomeric modifications.

The paraffins, as before remarked, form a chemically inert class of substances, not effected by sulphuric acid, nor even by nitric acid, or other powerful oxidising agents, at the ordinary cold. The normal paraffins occur in the distillation of coals and lignites, and are used in commerce for illumination, as kerosene, and fats, and for their lubricating properties. The solid members of the series form the paraffin tapers of commerce used for making candles.

METHANE,  $\text{CH}_4$  (methyl hydride, carburetted hydrogen), occurs naturally in coal-gas, where it is known as fire-damp, and also from stagnant pools, containing decaying organic matter; hence its synonym of *marsh gas*. It is obtained by passing the vapour of carbon disulphide with sulphuretted hydrogen, over heated copper,

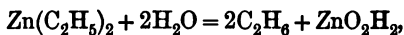
$\text{CS}_2 + 2\text{H}_2\text{S} + 4\text{Cu} = \text{CH}_4 + 4\text{CuS}$   
and also by heating sodium acetate with



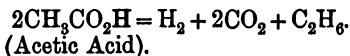
Marsh Gas is colourless, odourless, inflammable, and but sparingly soluble in water. It burns in excess of air, with a bluish-yellow, non-luminous flame, yielding carbonic acid and water as the sole products of combustion. When burnt with a limited supply of air a variety of products is formed, among which is acetylene,  $C_2H_2$ . Marsh gas forms a violently explosive mixture with air, and it is this property which renders it so dangerous in coal mines. The mixture of marsh gas and air requires a very high temperature for its ignition, and on the knowledge and application of this fact depends the safety in the use of Davy's lamp.

A mixture of marsh gas and chlorine explodes on exposure to direct sunlight, forming hydrochloric acid, and liberating carbon, thus:— $CH_4 + 4Cl = C + 4HCl$ . In ordinary diffused light the following products  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , and  $CCl_4$ , are formed:—

ETHANE,  $C_2H_6$  (Ethyl hydride), may be prepared by the action of water on zinc ethide,



or by submitting acetic acid to electrolysis, hydrogen being evolved at the negative pole, and carbonic anhydride and ethane at the positive pole,



The carbonic anhydride may be separated from the ethane by the action of caustic potash. Ethane is a colourless, inodourless, inflammable gas, very slightly soluble in water. It is converted by the action of chlorine in diffused daylight into the derivatives  $C_2H_5Cl$ ,  $C_2H_4Cl_2$ ,  $C_2H_3Cl_3$ , etc.

PROPANE,  $C_3H_8$ , may be obtained by the action of nascent hydrogen on propyl chloride. Very little is known of this compound in the free state.

TETRANE,  $C_4H_{10}$  — Rational formula =  $CH_3CH_2CH_2CH_3$ , — is a liquid prepared by exposing ethyl iodide over

mercury to bright sunlight,  $2\text{C}_2\text{H}_5\text{I}$   $\text{HgI}_2$ . It is the lightest of known, specific gravity of .60 and boiling at  $0^\circ$  modification, isopropylmethane, having mola  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$  is known.

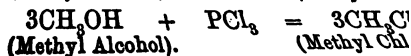
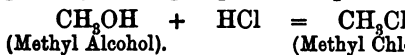
PENTANE,  $\text{C}_5\text{H}_{12} = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  boiling at  $38^\circ$ , obtained by fractional the lighter portions of petroleum oil modifications are known.

The higher members of the paraffin isolated by repeated fractional distillation of petroleum oil. The oil of commerce is a liquid hydrocarbons of the series, while paraffin is doubtless a mixture of higher series, but the formula of its composition is satisfactorily established. Its melting :  $40^\circ$  to  $60^\circ$ , and its boiling point is about

#### HALOID DERIVATIVES OF THE

The paraffins are acted on by chloro-ally under the influence of light. Bromine under similar conditions, but while iodine has no direct action.

The mono substitution derivatives can be prepared in a state of purity by the action of the halogens on the individual members. The fact that higher derivatives are simultaneously formed. Thus, when equal volumes of methane and chlorine are exposed to light,  $\text{CH}_3\text{Cl}$  is formed, accompanied by the higher derivatives and  $\text{CCl}_4$ . For this reason a different method of preparing these monoderivatives is adapted to the monohydric alcohols by halogenating with haloid phosphorus compounds



The di-derivatives of the paraffins are formed by acting on the  $C_nH_{2n}$  series with the halogens. Most of the higher haloid derivatives have been little studied.

The most important haloid derivatives of methane are as follow :—

**METHYL CHLORIDE** (monochloromethane),  $CH_3Cl$ , is the first product of the action of sunlight as a mixture of chlorine and methane, but is best prepared by saturating methyl alcohol,  $CH_3OH$ , with hydrochloric acid gas, and subsequently applying a gentle heat, when the methyl chloride is evolved as a colourless gas, which may be condensed at  $20^\circ$ . When methyl chloride is heated to  $100^\circ$ , in a closed tube with potash, potassium chloride and methyl alcohol are formed,  $CH_3Cl + KHO = CH_3OH + KCl$ . The iodide and bromide are colourless liquids, prepared by acting on methyl alcohol with phosphorus bromide and iodide respectively.

**DICHLOROMETHANE**,  $CH_2Cl_2$ , is a colourless liquid, boiling at  $40^\circ$  to  $42^\circ$ .

**TRICHLOROMETHANE**, **CHLOROFORM**,  $CHCl_3$ , may be obtained by the action of chlorine on methane, but is more conveniently prepared by the action of bleaching powder on methyl or ethyl alcohol, the latter compound being generally employed. It is prepared on a large scale by submitting a mixture of good commercial chloride of lime, alcohol, and water, to cautious distillation in a capacious retort. The product is then purified by agitation with water, treated with fused calcium chloride, and redistilled. Chloroform is a colourless mobile liquid, with a peculiarly sweet taste and smell. Its specific gravity is 1.5, and it boils at  $62^\circ$ . It is very slightly soluble in water, and is not affected by strong sulphuric acid. When heated in a closed tube with potash solution, a mixture of potassium chloride and potassium formate is produced. Chloroform is a most powerful anæsthetic, being largely employed in surgical operations, to produce

insensibility to pain. It is rapidly converted in the blood into formic acid, and may thus escape detection in cases of poisoning. Its use as an anæsthetic is likely to be superseded by its old rival, ether.

**TRI-IODIMETHANE.**—Iodoform,  $\text{CHI}_3$ , is a yellow crystalline substance, soluble in alcohol and ether, and is obtained by the action of iodine on alcohol in the presence of potassium hydrate.

**TETRA-CHLOROMETHANE.** — (Carbon tetra-chloride),  $\text{CCl}_4$ , is the final product of the action of chlorine on marsh gas, or on either of the compounds  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , or  $\text{CH}_3\text{Cl}$ . It is a colourless, heavy, mobile liquid, possessing anæsthetic properties, boiling at  $78^\circ$ , and having a specific gravity of 1.6. Carbon tetra-chloride, when placed in contact with sodium amalgam and water, is reduced by the evolved nascent hydrogen, to  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ , and finally to marsh gas.

Methane yields a nitro compound,  $\text{CH}_3(\text{NO}_2)$ , called *nitromethane*. This substance is obtained by the action of iodomethane, or silver nitrite. It is a heavy oily liquid of peculiar odour, and boils at  $99^\circ$ .

### $\text{C}_n\text{H}_{2n}$ , GROUP OF HYDROCARBONS. OLEFINES.

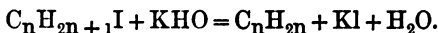
This series differs from the paraffin series, by containing two atoms less hydrogen. The following olefines have been obtained :—

NAME	FORMULA	BOILING POINT	NAME	FORMULA	BOILING POINT
Ethylene	$\text{C}_2\text{H}_4$	...	Octylene	$\text{C}_8\text{H}_{16}$	$120^\circ$
Propylene	$\text{C}_3\text{H}_6$	$18^\circ$	Nonylene	$\text{C}_9\text{H}_{18}$	$140^\circ$
Butylene	$\text{C}_4\text{H}_8$	$1^\circ$	Diamylene	$\text{C}_{10}\text{H}_{20}$	$160^\circ$
Iso-butylene	$\text{C}_4\text{H}_8$	$6^\circ$	Triamylene	$\text{C}_{15}\text{H}_{30}$	$240 \text{ to } 250^\circ$
Ethylallyl	$\text{C}_5\text{H}_{10}$	$32 \text{ to } 39^\circ$	Cetene	$\text{C}_{16}\text{H}_{32}$	$275^\circ$
Amylene	$\text{C}_5\text{H}_{10}$	$35^\circ$	Tetramylene	$\text{C}_{20}\text{H}_{40}$	$390 \text{ to } 400^\circ$
Hexylene	$\text{C}_6\text{H}_{12}$	$65^\circ$	Cerotene	$\text{C}_{27}\text{H}_{54}$	...
Heptylene	$\text{C}_7\text{H}_{14}$	$96^\circ$	Melene	$\text{C}_{30}\text{H}_{60}$	$375^\circ$

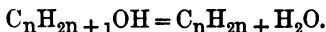
In this series it is to be noticed that the number of hydrogen atoms is exactly double the number of carbon atoms. As all the series contain two atoms of hydrogen less than the corresponding paraffins, which are saturated compounds, they are capable of uniting directly with chlorine or bromine to produce compounds which are di-haloid substitution derivatives of the paraffins. The olefines unite directly with sulphuric acid, to form *acid ethereal salts*, which yield on distillation with water a monohydric alcohol, containing the same number of carbon atoms as the olefine.

#### PRINCIPAL MODES OF FORMATION

There are several methods by which the members of this series may be obtained. The following will serve as examples:—(1.) By the action of an aqueous or alcoholic solution of potassium hydrate on the monohaloid derivatives of the corresponding paraffins, thus—



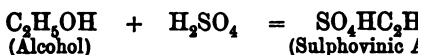
(2.) By the action of strong de-hydrating agents, such as concentrated sulphuric acid or phosphoric oxide, on the corresponding monohydric alcohols:—



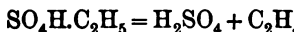
The following is a description of the preparation and properties of the most important members of the olefine series:—

ETHYLENE OR ETHENE,  $C_2H_4$  (Olefiant Gas, heavy carburetted hydrogen), may be directly prepared by the action of nascent hydrogen on acetylene,  $C_2H_2 + H_2 = C_2H_4$ . Olefiant gas is best prepared by the action of sulphuric acid on ordinary alcohol, at a temperature of about  $165^\circ$ . In practice a mixture of ten parts of concentrated sulphuric acid, and three parts of water, is heated to the required temperature in a

flask, and alcohol dropped slowly in; th is passed first through caustic soda solu from carbonic and sulphurous acids, through sulphuric acid to absorb ether water vapour. The first reaction which c the sulphuric acid and the alcohol, is the *sulphovinic acid*, thus :—



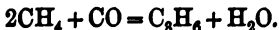
This being an unstable compound, rapid into ethylene and sulphuric acid, thus :—



Pure olefiant gas is colourless and odour sses a sweetish taste. It is almost water. It may be condensed by cold as the liquid form. It is very combustible, a bright white flame. Olefiant gas cc large extent the illuminating element of gas. It is decomposed by passage thro tube into carbon and marsh gas,  $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$ . Ethylene co with chlorine in diffused daylight to f chloride, or Dutch Liquid.

ETHYLENE CHLORIDE,  $\text{C}_2\text{H}_4\text{Cl}_2$ , is a co of agreeable ethereal odour, insoluble soluble in alcohol and ether. It boils a a specific gravity of 1.25. It is acted with formation of compounds having t  $\text{C}_2\text{H}_3\text{Cl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ ,  $\text{C}_2\text{HCl}_5$ , and  $\text{C}_2\text{Cl}_6$ , in w point steadily augments with the incre Ethylene also unites with bromine to bromide,  $\text{C}_2\text{H}_4\text{Br}_2$ , which is a colourless l iodine to form a white crystalline subs iodide,  $\text{C}_2\text{H}_4\text{I}_2$ .

PROPYLENE, or *Propene*,  $C_3H_6$ , may be prepared by passing marsh gas and carbonic oxide through a red-hot tube,



BUTYLENE,  $C_4H_8$ , is obtained by the action of potassium hydrate on iodotetrane.

AMYLENE, *Pentane*,  $C_5H_{10}$ , is obtained by heating amyl alcohol with aqueous solution of zinc chloride.

### $C_nH_{2n-2}$ GROUP OF HYDROCARBONS

#### THE ACETYLENE SERIES

Seven members of this group are known, but the only one which needs receive attention here is the first member, viz., acetylene.

ACETYLENE,  $C_2H_2$ .—Acetylene is a constant product of the incomplete combustion of many organic compounds. Its formation from the decomposition of ethylene has been already noticed. It may be formed by the direct union of its elements, but the required temperature is so high that the electric spark is the only available means which can be used. By the action of a powerful electric spark passing between two carbon terminals, placed in an atmosphere of hydrogen, a union of the carbon and hydrogen takes place, and acetylene is formed. The production of acetylene is important as showing the preparation of an organic substance from the direct union of its elements. By passing the mixture of hydrogen and acetylene through an ammoniacal solution of cuprous chloride, a red precipitate of cuprous acetylide is formed, which evolves pure acetylene when boiled with hydrochloric acid. Acetylene is a colourless gas of a peculiar and disagreeable odour, burning in the air with a bright smoky flame. It is present in small quantity in coal gas. The compounds which acetylene forms with such metals as copper and silver, are explosive in the dry state. Chlorine has



such a violent action on acetylene as to cause an explosion with separation of carbon. With bromine it forms the compounds  $C_2H_2Br_2$  and  $C_2H_2Br_4$ .

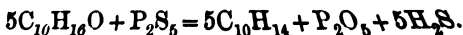
### $C_nH_{2n-4}$ SERIES OF HYDROCARBONS

#### THE TERPENES

Of this series only two members have been prepared synthetically, viz:—*Quintone*,  $C_5H_8$ , and *Decone*,  $C_{10}H_{16}$ . There are, however, a large number of volatile oils, called terpenes, having the empirical composition  $C_5H_8$ , which exist ready formed in such plants as the conifers, and in the order aurantiacea. One of the commonest and best known members of the group is ordinary oil of turpentine, which is obtained by distilling the oleo-resinous juice which exudes from the bark of different members of the coniferæ. One of the most singular characteristics of the terpenes is the large number of isomeric modifications which appear to exist among them, the essential oils of various plants often differing in physical properties, such as, specific gravity, boiling point, odour, etc., yet possessing the same percentage composition, and differing very slightly in their chemical behaviour. The natural terpenes are specially peculiar in the tendency which they exhibit to become converted into isomeric compounds, or into resinous oxidation products. Nearly all the terpenes have the composition  $C_{10}H_{16}$ , but some polymeric modifications are known which have the composition  $C_{20}H_{32}$ , and there is also an intermediate series, not strictly belonging to the group, but which may be conveniently noticed under the same heading, having the composition  $C_{15}H_{24}$ . The boiling points of the isomeric members of the  $C_{10}H_{16}$  group range from  $160^\circ$  to  $176^\circ$ . They are colourless mobile liquids. The  $C_{15}H_{24}$  group are viscid, of greater density, and boil at from  $249^\circ$  to  $260^\circ$ , while the  $C_{20}H_{32}$  group are very viscid, and boil at above

300°. Natural essential oils are generally colourless, possess a characteristic odour, mix with the fat oils, are soluble in alcohol and ether, and on exposure to air slowly absorb oxygen, and become more or less resinous. They are generally prepared from plants which contain them by pressure or by distillation with water.

The best known isomeric modifications of the natural terpenes are—*Terebenthene*, obtained from the *Pinus maritima*, and *Austraterebenthene*, obtained from *Pinus australis*. Both varieties boil at 161°, but the first turns the plane of a ray of polarised light to the left, while the second turns it to the right. Terebenthene forms a crystalline hydrate with water, and combines with hydrochloric acid. Iodine acts violently on it, forming, when the action is moderated, hydriodic acid and cymene,  $C_{10}H_{14}$ . The essential oils are isomers of turpentine, often containing certain quantities of oxidised oils. As examples of essential oils may be mentioned the oils of lemon, carraway, cammomile, lavender, cloves, etc.; these form, by oxidation, resins and camphors. The best known of the latter class of substances is common camphor,  $C_{10}H_{16}O$ , a crystalline body obtained from the *Laurus camphora*. It is generally met with as a white, semi-transparent, crystalline mass, which fuses at 175°, and boils at 204°. It turns the plane of polarization to the right, but a modification is known possessing an entirely contrary action. Camphor is soluble in alcohol, and also in alcoholic potash. When the last named solution is heated, the camphor is first converted into *Borneo camphor* or *Borneol*,  $C_{10}H_{18}O$ , a product occurring naturally in the bark of *Dryabalanops camphora*. On continuing the heat, *camphinic acid* is formed,  $C_{10}H_{16}O_2$ , and subsequently *campholic acid*,  $C_{10}H_{18}O_2$ . By boiling camphor with nitric acid, *camphoric acid*,  $C_{10}H_{16}O_4$ , is formed, while if heated with phosphorus pentasulphide, *cymene* is produced,



Resins and balsams are oxidation products of the terpenes, of which common resin is a familiar example.

Common resin is left as a residue from the distillation of crude turpentine. Other well known resins, such as shellac, mastic, copal, etc., have a similar composition. Caoutchouc, or India rubber, and gutta-percha, are further examples of this class of substances. Caoutchouc is the hardened juice of several tropical trees, such as the *Siphonia elastica* and *Jatropha elastica*. It is white when pure, the black colour of the commercial article being derived from the smoke of the fires employed in drying. Gutta-percha is obtained from the *Isonandra gutta*, growing in Singapore and Borneo. *Vulcanised India-rubber* and *Ebonite* are produced by heating caoutchouc with sulphur. Both caoutchouc and gutta-percha are insoluble in alcohol, but dissolve in turpentine, carbon disulphide, chloroform, and ether.

### $C_nH_{2n-6}$ GROUP OF HYDROCARBONS

#### THE BENZENE SERIES

The Benzene series of hydrocarbons possess properties which distinguish them completely from the preceding nonsaturated groups. Whereas the members of the previously mentioned groups are all capable of uniting with chlorine or bromine to form additive compounds, the benzene series seem to act in most cases as perfectly saturated hydrocarbons, which form by the action of the halogens substitution derivatives, in preference to additive compounds. The members of the benzene series are also characterised by their extreme stability, and by the number of well-defined substitution derivatives which they afford. From the aromatic odour possessed by many of these derivatives, the benzene series of hydrocarbons are frequently spoken of as the aromatic group. Hydrocarbons of the benzene series are found in small quantities in ess-

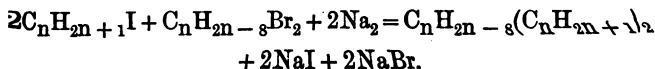
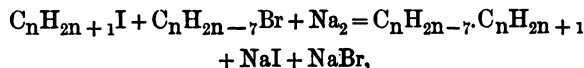
ciation with the paraffins in petroleum oil, but their chief source is the tar produced as a bye-product of the destructive distillation of coal in the manufacture of coal gas. The benzene series afford a remarkable number of isomeric modifications, the starting point of the group being benzene,  $C_6H_6$ . The following are some of the members of this group:—

NAME	FORMULA	BOILING POINT
Benzene	$C_6H_6$	81°
Methyl benzene (toluene)	$C_7H_8$	111°
Ethyl benzene	$C_8H_{10}$	135°
Propyl benzene (Cumene)	$C_9H_{12}$	157°
Isobutyl benzene (Cymene)	$C_{10}H_{14}$	159 to 161°
Isoamyl benzene	$C_{11}H_{16}$	193°
Isoamyl methyl benzene	$C_{12}H_{18}$	213°
Isoamyl dimethyl benzene	$C_{13}H_{20}$	232°

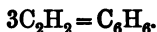
No member of this group has been obtained by a purely chemical and connected series of reactions from the corresponding paraffin, and no hydrocarbon of the series has yet been discovered containing less than six atoms of carbon.

#### PRINCIPAL MODES OF PRODUCTION

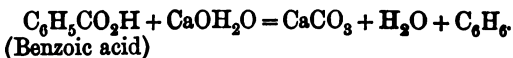
By acting on a moniodated paraffin with a brominated derivative of benzene, or an homologous hydrocarbon with sodium.



**BENZENE**,  $C_6H_6$  (Benzol. Phenyl Hydride), may be obtained by the action of heat on acetylene.



Benzene is also produced by the passage of its higher homologues, through a red-hot tube. It may be best procured by distilling benzoic acid with slaked lime at a dull red heat.



Benzene is prepared on a large scale for the manufacture of aniline colours, by the redistillation of the lighter oils obtained from coal tar, which boil below  $100^\circ$ . Pure benzene is a colourless limpid liquid, boiling at  $81^\circ$ , and having a specific gravity of  $\cdot 899$ . It solidifies to a brilliant white crystalline mass at  $0^\circ$ . It is almost insoluble in water. Benzene, when acted on by chlorine in direct sunlight, forms the additive compound  $C_6H_6Cl_6$ . It also forms a regular series of substitution derivatives by the action of chlorine, assisted by gentle heat. The first of these is the compound  $C_6H_5Cl$ , which boils at  $133^\circ$ , and the last is the compound  $C_6Cl_6$ , boiling at  $326^\circ$ . When treated with nitric acid, nitrobenzene,  $C_6H_5(NO_2)$ , is formed, which, in contact with reducing agents, is converted into aniline,  $C_6H_5(NH_2)$ .

**TOLUENE**,  $C_7H_8 = C_6H_5CH_3$  (Methyl benzene), is generally obtained from the fractional distillation of the portions of coal tar oil boiling between  $100^\circ$  and  $120^\circ$ . It may also be prepared from benzol, by replacing one atom of hydrogen by methyl. Toluene is a colourless mobile liquid, of specific gravity  $\cdot 881$ , boiling at  $111^\circ$ . It furnishes benzoic acid by oxidation, and by the action of nitric acid, nitrotoluene,  $C_7H_7(NO_2)$ .

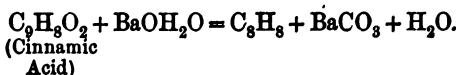
**CUMENE**,  $C_9H_{12}$ , occurs in Roman cumin oil, and a compound, cumene, containing three isomeric trimethyl benzenes, occurs in coal tar.

$C_nH_{2n-8}$  GROUP OF HYDROCARBONS

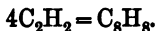
Three hydrocarbons of this series are known, viz.—

Cinnamene	.	.	.	$C_8H_8$
Allyl-benzene	.	.	.	$C_9H_{10}$
Phenyl-butylene	.	.	.	$C_{10}H_{12}$

The most important of these is cinnamene, which is present in liquid storax, and may be separated by distilling the balsam with water. Cinnamene may also be obtained by distilling cinnamic acid with barium hydrate.



It is likewise formed when acetylene is strongly heated.



Pure cinnamene is a colourless mobile liquid, boiling at  $145^\circ$ , and combining directly with chlorine and bromine to form the additive compounds  $C_8H_8Cl_2$  and  $C_8H_8Br_2$ .

 $C_nH_{2n-10}$  GROUP OF HYDROCARBONS

Only one member of this series is known, viz., acetenyl-benzene,  $C_8H_6$ . It is a colourless liquid of aromatic odour, and boils at  $139^\circ$ . It may be obtained by heating phenylpropionic acid with water to  $120^\circ$  ( $C_9H_8O_2 = CO_2 + C_8H_6$ ).

 $C_nH_{2n-12}$ ,  $C_nH_{2n-18}$ , AND  $C_nH_{2n-24}$  GROUPS OF HYDROCARBONS

These hydrocarbons are represented by one member for each series. Naphthalene ( $C_{10}H_8$ ), is the representative of the first series; anthracene ( $C_{14}H_{10}$ ), of the second; and chrysene ( $C_{18}H_{12}$ ), of the third. They

may be regarded as members of a series differing from each other by  $C_4H_2$ , and of which benzene,  $C_6H_6$ , is the first member. Benzene and this series exhibit, in fact, similarities in chemical behaviour, the leading feature in common being the production of *quinones* on oxidation. Most hydrocarbons on oxidation have two constituent hydrogen atoms replaced by one of oxygen, but in these quinones, *two* atoms of oxygen are introduced for every two atoms of hydrogen withdrawn. The quinones are neutral bodies, and are converted by nascent hydrogen into hydroquinones.

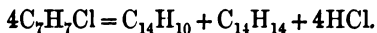
NAPHTHALENE,  $C_{10}H_8$ , the representative member of the  $C_nH_{2n-12}$  series, is one of the bye-products in the manufacture of coal gas, occurring to a large extent in coal tar, and is a constant product of the decomposition of hydrocarbons, and organic substances generally, at a high temperature. Naphthalene is a white solid substance, crystallising in pearly plates. It is very volatile, passing into vapour readily at ordinary temperatures; it melts at  $80^\circ$ , and boils at  $217^\circ$ . It possesses a peculiar odour, is insoluble in water, but soluble in alcohol, ether, the essential and fat oils, and in acetic acid. Naphthalene forms numerous compounds with chlorine, giving both substitution derivatives and additive compounds. With nitric acid four compounds are formed, viz., nitronaphthalene,  $C_{10}H_7NO_2$ , and di-, tri-, and tetra-nitronaphthalene; while, when exposed to the oxidising action of chromic anhydride, naphthoquinone,  $C_{10}H_6O_2$ , is formed. By treatment with reducing agents, nitronaphthalene yields naphthylamine,  $C_{10}H_7NH_2$ , which, like aniline, yields coloured oxidation products.

By the continued action of nitric acid on naphthalene, phthalic acid,  $C_8H_6O_4$ , is formed, which, when heated with excess of lime or baryta, yields benzene. Naphthalene is dissolved by warm sulphuric acid, naphthalene-sulphonic acid,  $C_{10}H_7HSO_3$ , being formed. A yellow dye, called naphthalene yellow, consists of

dinitro-naphthol,  $C_{10}H_5(NO_2)_2OH$ , a nitro-substitution derivative of naphthol,  $C_{10}H_7OH$ .

Naphthalene has two homologues, viz., methyl-naphthalene,  $C_{10}H_7CH_3$ , and ethylnaphthalene,  $C_{10}H_7C_2H_5$ .

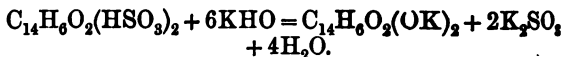
ANTHRACENE,  $C_{14}H_{10}$ , is the leading member of the  $C_nH_{2n-18}$  series of hydrocarbons. It is obtained from the least volatile portions of coal tar, and has lately become of great importance from the discovery that alizarin, the colouring principle of madder, can be prepared from it. Anthracene crystallises in white scales, melts at  $213^\circ$ , and boils at about  $360^\circ$ . It may be prepared artificially by heating benzyl-chloride,  $C_7H_7Cl$ , in a closed vessel, with water to  $200^\circ$ , when it forms anthracene, benzyltoluene,  $C_{14}H_{14}$ , and hydrochloric acid, thus—



Anthracene forms substitution products with bromine and chlorine, and by the action of oxidising agents, yields anthraquinone,  $C_{14}H_8O_2$ . By the action of bromine on anthraquinone, dibromanthraquinone is formed, which, when heated with potassium hydrate, yields the potassium derivative of alizarin, from which the alizarin may be prepared by the action of an acid. Alizarin is the most interesting and most important derivative of anthracene, for its preparation is the first instance of the production of a natural colouring principle by artificial means. Alizarin is now manufactured on a large scale for use as a dye. The anthracene is converted by the action of chlorine into dichloranthracene,  $C_{14}H_8Cl_2$ . By heating this compound with excess of sulphuric acid, dichloranthracene-disulphonic acid,  $C_{14}H_6Cl_2(HSO_3)_2$ , is formed, which, by the action of nitric acid or other oxidising agents, is converted into anthraquinone-disulphonic acid,  $C_{14}H_6O_2(HSO_3)_2$ .



which, by heating with caustic potash to  $180^{\circ}$ , yields the potassium derivative of alizarin and potassium sulphite.



By treating the aqueous solution of the potassium derivative with acid, the crude alizarin is precipitated, and may be purified by careful sublimation, yielding beautiful red prisms. Alizarin dissolves in alkalis and alkaline carbonates, forming deep purple solutions.

CHRYSENE,  $\text{C}_{18}\text{H}_{12}$ , the only known hydrocarbon of the  $\text{C}_n\text{H}_{2n-24}$  series, occurs in coal tar. It crystallises in small yellow scales, melting at  $246^{\circ}$ .

#### $\text{C}_n\text{H}_{2n-14}$ GROUP OF HYDROCARBONS

Several members of this series are known, among which may be mentioned diphenyl,  $\text{C}_{12}\text{H}_{10}$ , ditoluene  $\text{C}_{14}\text{H}_{14}$ , and dibenzyl,  $\text{C}_{14}\text{H}_{14}$ . Diphenyl,  $\text{C}_6\text{H}_5\text{C}_6\text{H}_5$ , is formed by passing benzene vapour through a red-hot tube,  $2\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + \text{H}_2$ . It forms beautiful white crystalline plates, which melt at  $70^{\circ}$ . It yields benzoic acid on oxidation.

#### $\text{C}_n\text{H}_{2n-16}$ GROUP OF HYDROCARBONS

Only one member of this series is known, viz., stilbene or toluyene,  $\text{C}_{14}\text{H}_{12}$ . It is formed by passing the vapour of dibenzyl through a red-hot tube.

#### $\text{C}_n\text{H}_{2n-22}$ GROUP OF HYDROCARBONS

Two members of this series, having the composition  $\text{C}_{16}\text{H}_{10}$ , viz., diacetonylbenzene and pyrene, are known. A third member, diphenylbenzene, has the composition  $\text{C}_{18}\text{H}_{14} = \text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ ; and a fourth mem-

ber is triphenylmethane,  $C_{19}H_{14}$ . All these compounds are chiefly remarkable for the large amount of carbon which they contain. One of the group, viz., pyrene, is a constituent of coal tar; it crystallises in colourless plates, which melt at  $142^\circ$ , and much resembles anthracene.

### $C_nH_{2n-32}$ GROUP

The representative member of this group is tetraphenylethylene,  $C_2(C_6H_5)_4$ . It is crystalline, and melts at  $220^\circ$ .

## ALCOHOLS

The alcohols may be regarded as derived from the hydrocarbons, by the substitution of the hydroxyl group (OH) for hydrogen, and are monohydric, dihydric, trihydric, etc., according to the number of hydrogen atoms of the original hydrocarbon which are so replaced.

The following table gives the monohydric alcohols of the general formula  $C_nH_{2n+1}OH$ . They are sometimes called the *normal* or *primary* alcohols:—

		Boiling Point
Methyl alcohol . . .	$CH_3, OH$	$66^\circ$
Ethyl " . . .	$C_2H_5, OH$	$78.4^\circ$
Propyl " . . .	$C_3H_7, OH$	$97.5^\circ$
Teteryl or butyl alcohol	$C_4H_9, OH$	$116^\circ$
Pentyl or amyl " . .	$C_5H_{11}, OH$	$137^\circ$
Hexyl alcohol . . .	$C_6H_{13}, OH$	$157^\circ$
Heptyl " . . .	$C_7H_{15}, OH$	$176^\circ$
Octyl " . . .	$C_8H_{17}, OH$	$195^\circ$
Nonyl " . . .	$C_9H_{19}, OH$	
Cetyl " . . .	$C_{16}H_{33}, OH$	
Cerotic " . . .	$C_{27}H_{55}, OH$	
Melissic " . . .	$C_{30}H_{61}, OH$	

These *primary* alcohols yield two classes of isomers, so that the whole series of these alcohols can be divided into three groups, known respectively as the primary, secondary, and tertiary alcohols.

The following is a list of the normal secondary alcohols:—

			Boiling Point
Dimethyl carbinol	$\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	83°
Ethyl-methyl-carbinol	$\begin{matrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	99°
Propyl-methyl-carbinol	$\begin{matrix} \text{CH}_3 \\ \text{C}_3\text{H}_7 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	120°
Teteryl-methyl-carbinol	$\begin{matrix} \text{CH}_3 \\ \text{C}_4\text{H}_9 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	137°
Pentyl-methyl-carbinol	$\begin{matrix} \text{CH}_3 \\ \text{C}_5\text{H}_{11} \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	160-162°
Dipropyl-carbinol	$\begin{matrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	150°
Hexyl-methyl-carbinol	$\begin{matrix} \text{CH}_3 \\ \text{C}_6\text{H}_{13} \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{CH.OH}$	181°

The following list gives the normal tertiary alcohols:—

			Boiling Point
Trimethyl-carbinol	$(\text{CH}_3)_3$	COH	82.5°C
Ethyl-dimethyl-carbinol	$\begin{matrix} (\text{CH}_3)_2 \\ \text{C}_2\text{H}_5 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{COH}$	98.5°
Propyl-dimethyl-carbinol	$\begin{matrix} (\text{CH}_3)_2 \\ \text{C}_3\text{H}_7 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{COH}$	115°
Diethyl-methyl-carbinol	$\begin{matrix} (\text{CH}_3) \\ (\text{C}_2\text{H}_5)_2 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{COH}$	120°
Triethyl-carbinol	$(\text{C}_2\text{H}_5)_3$	COH	141°
Propyl-diethyl-carbinol	$\begin{matrix} (\text{C}_2\text{H}_5)_2 \\ \text{C}_3\text{H}_7 \end{matrix}$	$\left. \begin{matrix} \\ \end{matrix} \right\} \text{COH}$	Partially decomposes on boiling

The term carbinol as applied to the alcohols was proposed by Professor Kolbe. Methyl alcohol is called carbinol simply,  $\text{CH}_3\text{OH}$ ; ethyl alcohol is methyl carbinol,  $\text{CH}_3\text{CH}_2\text{OH}$ ; and the higher alcohols are

regarded as having hydrogen replaced by a monad group of the form  $C_nH_{2n+1}$ , thus—

Methyl-carbinol  $(CH_3)CH_2(OH)$  = Ethyl alcohol

Ethyl-carbinol  $(C_2H_5)CH_2(OH)$  = Propyl alcohol

Propyl carbinol  $(C_3H_7)CH_2(OH)$  = Butyl alcohol

The three series of monohydric alcohols may then be represented in general terms as follow, carbinol being  $CH_3OH$  :—

Primary carbinol  $CH_2(C_nH_{2n+1})OH$

Secondary carbinol  $CH(C_nH_{2n+1})_2OH$

Tertiary carbinol  $C(C_nH_{2n+1})_3OH$

The three classes of alcohols are distinguished by their reactions on oxidation. The boiling points of the primary alcohols are higher than those of the secondary, and these are again higher than those of the tertiary.

#### THE PRIMARY MONOHYDRIC ALCOHOLS

These are distinguished by their producing on oxidation—first, an *aldehyde*, and on further oxidation, an *acid*, having the same number of carbon units as the alcohol. In most cases the acid formed reacts on the unaltered alcohol to form a compound ether. The primary monohydric alcohols may be conveniently represented on the water type  $\begin{matrix} H \\ | \\ H \end{matrix} \} O$ , in which one hydrogen atom is replaced by the alcohol radical, thus—

Methyl alcohol  $\begin{matrix} H \\ | \\ CH_3 \end{matrix} \} O$ , Ethyl alcohol  $\begin{matrix} H \\ | \\ C_2H_5 \end{matrix} \} O$ .

Propyl alcohol  $\begin{matrix} H \\ | \\ C_3H_7 \end{matrix} \} O$ .

The primary alcohols are produced when the monochlorinated derivative of the corresponding paraffin is acted on by silver or sodium acetate, by which the chlorine of the derivative is withdrawn, while the radical of the derivative forms an ethereal salt or compound ether with the acetic acid. By the action of

potassium hydrate on the ethereal salt, potassium acetate is produced, together with the required alcohol. The following is a description of the preparation and properties of the leading primary monohydric alcohols of the series  $C_nH_{2n+1}OH$ —the ethylic series :—

### METHYL ALCOHOL OR CARBINOL

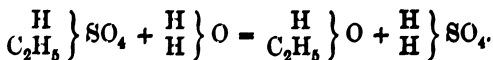
$\left. \begin{array}{l} H \\ CH_3 \end{array} \right\} O\text{—or } CH_3OH.$  This substance is generally known as *wood spirit*, or *pyroxylic spirit*. It occurs in the products of the destructive distillation of wood, and may be obtained by treating the oil of winter-green (*Gaultheria procumbens*), which consists of methyl-salicylate, with caustic potash :—



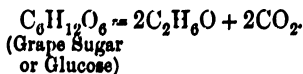
Methyl salicylate. Potassium salicylate.

Pure methyl alcohol may be prepared from crude wood spirit by treating it with oxalic acid, by which treatment crystalline methyl oxalate is formed,  $\left. \begin{array}{l} CH_3 \\ CH_3 \end{array} \right\} C_2O_4.$  On treatment with water, this substance is decomposed, and yields the alcohol, which may be obtained in the pure state by distillation with quick lime. Methyl alcohol, in the crude condition of wood spirit, possesses an offensive odour and taste, but the pure substance closely resembles common or ethyl alcohol in taste and smell. It is a colourless mobile liquid, of specific gravity 0.814 at 0°, boiling at 66°, and soluble in, and miscible with, water, in all proportions. It is inflammable, burning with a bluish non-luminous flame. By oxidation it yields formic acid. The *methylated spirit* of commerce consists of a mixture of 90 per cent. of ordinary alcohol, with 10 per cent. of partially purified wood spirit. This mixture is sold free of duty for industrial purposes, such as the manufacture of varnishes.

ETHYL ALCOHOL, or *Methyl-Carbinol*,  $\left. \begin{smallmatrix} \text{H} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$ , or  $\text{CH}_3\text{CH}_2\text{OH}$ , is better known as *Alcohol*, or *Spirits of Wine*. This substance is remarkable from the fact that it can be prepared by the direct union of its elements, which is accomplished as follows:—Acetelyne,  $\text{C}_2\text{H}_2$  (see page 381), may be prepared from its elements, and combines directly with two atoms of hydrogen to form olefiant gas,  $\text{C}_2\text{H}_4$ . By acting on olefiant gas with strong sulphuric acid, sulphovinic acid, or hydrogen-ethyl-sulphate is formed,  $\left. \begin{smallmatrix} \text{H} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{SO}_4$ , which, when boiled with water, yields sulphuric acid and alcohol, thus—



Alcohol may also be produced from olefiant gas by first converting the latter into ethyl iodide by the action of hydriodic acid, and subsequently decomposing the ethyl iodide with potassium hydrate. Alcohol is always prepared on a large scale by the fermentation of sugar derived from various sources. A weak saccharine solution is mixed with “yeast,” an organised structure, which in the act of life and growth has the property of converting sugar into alcohol and carbonic acid—



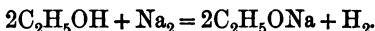
Where cane sugar is used, it passes first into grape sugar by assimilation of the elements of water. In order to separate the alcohol from the fermented liquid, distillation is resorted to, the alcohol boiling at a lower temperature than water, and thus coming over first. By collecting the first products of the distillation apart, and subsequently “rectifying” or re-distilling,

a spirit is at length obtained containing about 13 per cent. of water. In order to separate the water entirely from the alcohol, the rectified product is re-distilled with dry potassium carbonate or quick lime, the spirit then obtained being termed "absolute" alcohol. Pure ethyl alcohol is a colourless mobile liquid, of pungent and agreeable taste and odour. Its specific gravity is  $\cdot 7958$  at  $15\cdot 5^{\circ}$ , and it boils at  $78\cdot 4$  (with the barometer at 760 m.m.). From the fact of its not freezing by exposure to the lowest attainable temperature, it is employed for thermometers to indicate extreme degrees of cold. By exposure to a very low temperature ( $-100^{\circ}$ ) it becomes viscid. It is very inflammable, burning with a bluish non-luminous flame. It is extremely hygroscopic, attracting moisture with great avidity, and being miscible in all proportions with water. Direct dilution with water causes the evolution of heat, a contraction in volume also occurring. The specific gravities of known mixtures of alcohol and water have been carefully ascertained and tabulated, so that the percentage of absolute alcohol in a mixture of alcohol and water (free from other substances) can be at once ascertained by taking the specific gravity. This method is employed for ascertaining the strength of the various spirits of commerce, gin, whisky, etc. As alcohol expands considerably for any increase of temperature, a correction has generally to be made in the specific gravity determination. The various spirituous liquids, wine, beer, etc., owe their intoxicating effects to the presence of alcohol.

The following table shows the percentage of alcohol in the various spirituous liquids of commerce :—

Proof Spirit	Brandy, Whisky, and other Spirits	Strong Wines, Port, Sherry, &c.	Light Wines, Clarets, Hocks, &c.	Strong Beers	Ordinary Beers
50·8	40 to 50	15 to 20	7 to 10	6 to 9	4 to 6

In the estimation of the amount of alcohol in spirituous liquids which, like beer and wine, contain substances which would interfere with the correctness of an estimation of the alcoholic strength from the specific gravity, the liquid is subjected to distillation, and the amount of alcohol present obtained from the specific gravity of the distillate. Alcohol can take the place of water of crystallisation in certain salts, and such compounds are called alcoholates; they are decomposed by water. Alcohol is decomposed by passing it in a state of vapour through a red-hot tube, the chief products formed being hydrogen, marsh gas, olefiant gas, naphthaline, and benzole; when subjected to gradual oxidation, aldehyde,  $C_2H_4O$ , is first formed, and finally acetic acid,  $C_2H_4O_2$ . Potassium and sodium rapidly attack alcohol with evolution of hydrogen, and formation of potassium or sodium ethylate—



The haloid acids react on alcohol with formation of ethyl chloride, bromide, or iodide and water. With strong sulphuric acid, sulphovinic acid or hydrogen-ethyl-sulphate is produced, which forms compounds with bases called ethyl sulphates.

PROPYL ALCOHOL,  $C_3H_7OH = \left. \begin{matrix} C_3H_7 \\ H \end{matrix} \right\} O$ , exists in two isomeric modifications, distinguished as normal propyl alcohol, or ethyl carbinol,  $C_2H_5CH_2OH$ , and isopropyl alcohol, or dimethyl carbinol,  $C(CH_3)_2H.OH$ ; the first is a primary and the latter a secondary alcohol. The normal alcohol has been isolated from the products of the fermentation of grain, chiefly in the distillation of French brandies, and from the spirit obtained by the distillation of cider; it is a colourless liquid, which boils at  $96^\circ$ , and dissolves freely in water. It yields by oxidation propionic aldehyde and propionic acid, and unites with sulphuric acid to form hydrogen-propyl-sulphate. The general compounds resemble those



of ethyl alcohol. The secondary alcohol is obtained from isopropyl iodide, a product of the action of hydriodic acid upon glycerine; it boils at  $84^{\circ}$ .

BUTYL ALCOHOL,  $C_4H_9OH = \begin{matrix} C_4H_9 \\ H \end{matrix} \} O$ , exists in four isomeric modifications, which differ in their boiling points, and in the way in which they undergo decomposition, and more especially in their behaviour on oxidation. The normal alcohol, propyl carbinol, may be obtained from butyl-chloride. It yields on oxidation butyl aldehyde and butyric acid.

AMYL ALCOHOL,  $C_5H_{11}OH = \begin{matrix} C_5H_{11} \\ H \end{matrix} \} O$ , exists in six isomeric modifications. The normal alcohol occurs in the products of distillation of potato brandy, and is known as fousel or fusel oil. It is a colourless liquid, possessing a penetrating and disagreeable odour; it is not miscible with water, but is soluble in alcohol and ether. It boils at  $132^{\circ}$ , and solidifies at  $-20$ . Ordinary fusel oil contains two isomeric modifications, which are identical in chemical properties, but differ in their action on polarised light; the one being inactive, and the other turning the ray to the left. Both alcohols yield valeric acid on oxidation, and, like the preceding alcohols, unite with sulphuric acid to form hydrogen-amyl-sulphate, which forms salts called amyl sulphates. Potassium and sodium act upon amyl alcohol in the same way as on ethyl alcohol; and the bromide and iodide are also prepared in a similar way.

HEXYL ALCOHOL,  $C_6H_{14}O = \begin{matrix} C_6H_{13} \\ H \end{matrix} \} O$ , exists as butyrate in the essential oil of *Heracleum giganteum*. It boils at  $157^{\circ}$ . Heptyl alcohol,  $\begin{matrix} C_7H_{15} \\ H \end{matrix} \} O$ , is known.

Octyl Alcohol,  $\begin{matrix} C_8H_{17} \\ H \end{matrix} \} O$ , exists as acetate in the seeds of *Heracleum spondylium*. The secondary alcohol is

obtained by heating castor oil with potash. *Cetyl Alcohol*,  $C_{16}\frac{H_{33}}{H}$  } O, *Cerotic Alcohol*,  $C_{27}\frac{H_{51}}{H}$  } O, and *Melissic Alcohol*,  $C_{30}\frac{H_{61}}{H}$  } O, are obtained respectively by saponifying spermaceti, Chinese wax, and myricin. They are white crystalline substances, capable of forming chlorine derivatives by the substitution of Cl for (OH). They yield their corresponding acids on oxidation.

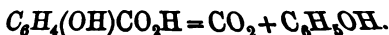
#### $C_nH_{2n-1}OH$ GROUP OF MONOHYDRIC ALCOHOLS

This series of alcohols bears the same relation to the olefines that the ethylic series bears to the paraffins. Two members of the series are known—*vinyl alcohol*,  $C_2H_3OH$ , and *allyl alcohol*,  $C_3H_5OH$ . Of these two, allyl alcohol is the most important. It is produced by heating glycerine with oxalic acid, and is a colourless liquid, of specific gravity .87, boiling at 96°, and possessing an irritating odour. The sulphocyanate of this alcohol,  $C_3H_5(NCS)$ , is formed by macerating black mustard seed with water, while garlic contains an offensive smelling oil, which is a sulphide of allyl,  $(C_3H_5)_2S$ .

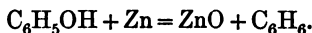
#### $C_nH_{2n-7}OH$ GROUP OF MONOHYDRIC ALCOHOLS

This group includes the phenols and alcohols of the benzyl series. These alcohols exhibit, to a greater degree even than the benzene series of hydrocarbons, the behaviour as saturated compounds, and the tendency to form substitution in place of additive compounds. The most important member of the series is benzene alcohol,  $C_6H_5OH$  (Phenol).

PHENOL (CARBOLIC ACID),  $C_6H_5OH = C_6\frac{H}{H_5}$  } O, may be obtained by distilling oxybenzoic acid with caustic lime—



Phenol is prepared on a large scale from coal tar. It is a white crystalline substance, melting at  $35^{\circ}$ , and boiling at  $184^{\circ}$ . It is very sparingly soluble in water, but dissolves freely in alcohol, ether, and acetic acid; also in alkalis, with which it forms phenates. It possesses a peculiar odour, and has a caustic action on the skin. Its most valuable property is its eminently antiseptic character, and hence it is much used as a disinfectant. Phenol suffers but little change when passed through a red-hot tube, but by heating it with zinc dust, benzene is produced—



Phenol is acted upon by chlorine, the final product formed being pentachlorophenol,  $\text{C}_6\text{Cl}_5\text{OH}$ . It is violently attacked by nitric acid, compounds being formed in which one, two, or three equivalents of hydrogen are replaced by  $\text{NO}_2$ . The final product,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ , tri-nitro-phenol, or picric acid, is a bright yellow crystalline substance, used for dyeing silk. Phenol is converted by the action of chromic acid into phenoquinone.

CRESOL (CRESILIC ACID),  $\text{C}_7\text{H}_7\text{OH} = \left. \text{C}_7\text{H}_7 \right\} \text{O}$ , is a crystalline solid, found in the crude carbolic acid obtained from coal tar. It boils at  $203^{\circ}$ . Three modifications are known, viz., paracresol, metacresol, and orthocresol. *Benzyl alcohol*,  $\text{C}_6\text{H}_5\text{CH}_2(\text{OH})$ , is metameric with cresol. It may be prepared by the action of an alcoholic solution of potash, or benzoic aldehyde. It is a colourless liquid, boiling at  $206^{\circ}$ .

#### $\text{C}_n\text{H}_{2n-9}\text{OH}$ GROUP OF MONOHYDRIC ALCOHOLS

Of this series two members are known. Cinnamic alcohol,  $\text{C}_9\text{H}_9\text{OH} = \left. \text{C}_9\text{H}_9 \right\} \text{O}$ , is obtained by heating styracine,  $\text{C}_9\text{H}_7\text{O}_2\text{C}_9\text{H}_9$ , with potash solution. Styra-

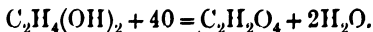
cine occurs as a constituent of liquid storax, and balsam of Peru. Cinnamic alcohol is a solid, crystallising in silky needles, melting at  $33^{\circ}$ , and yielding cinnamic aldehyde on oxidation. The other member of this series is cholesterin,  $C_{26}H_{48}OH$ , a crystalline substance found in the animal system (see chapter on Animal Chemistry).

### $C_nH_{2n}(OH)_2$ SERIES OF ALCOHOLS (DIHYDRIC)

#### THE GLYCOLS

The glycols may be regarded as the dihydroxyl derivations of the paraffins. Several members of the series have been obtained, the most important of which is *ethylene*, or *ethene glycol*,  $C_2H_4 \begin{Bmatrix} OH \\ OH \end{Bmatrix}$ . The glycols are colourless, somewhat viscid liquids, soluble in water and alcohol, and yield oxacids on oxidation.

Ethylene glycol or alcohol, is obtained by preparing glycol diacetate (by acting on ethylene dibromide by silver acetate), and subsequently acting on the glycol diacetate with baryta. Glycol is a thick colourless liquid, without odour, and possessing a sweetish taste. It has a specific gravity of 1.125 at  $0^{\circ}$ , boils at  $197^{\circ}$ , and is soluble in water and alcohol. By oxidation, it yields glycollic acid, and when treated with hot nitric acid, yields oxalic acid—



Glycol yields by the action of sodium, or potassium, products which are similar to those obtained under similar conditions from ethyl-alcohol, and it also forms an analogous product with sulphuric acid (glycol-sulphuric acid). It differs from ordinary alcohol, however, in yielding two acids.

$C_nH_{2n-8}(OH)_2$  GROUP OF DIHYDRIC ALCOHOLS

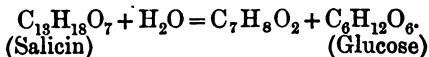
*Orcins, Aromatic Glycols, and Alcohols of the Saligenin Series.*

These alcohols are derived from the  $C_nH_{2n-6}$  series of hydrocarbons. The orcins, aromatic glycols, and alcohols of the saligenin series, are metameric compounds.

ORCIN,  $C_6H_3(CH_3)(OH)_2$ , exists in the lichens used for the preparation of litmus, archil, and cudbear. It forms six-sided colourless prisms, soluble in water, and melting at  $86^\circ$ . By the combined action of ammonia and oxygen, orcin is converted into orcein,  $C_7H_7NO_3$ , a non-crystalline colouring matter, soluble in alcohol, forming a deep scarlet solution, and also dissolving in solutions of alkalis, with which it forms a violet colour. Orcein is one of the colouring matters of commercial archil. The colour of litmus is no doubt an oxidation product of orcein.

PYRO-CATECHIN, OR OXYPHENOL,  $C_6H_4 \begin{smallmatrix} OH \\ OH \end{smallmatrix}$ , } is obtained by the dry distillation of catechin, and may also be produced by the action of potash on iodophenol,  $C_5H_4I(OH)$ . It crystallises from its solution in plates, which melt at  $116^\circ$ . Pyro-catechin is isomeric with two other compounds, viz. :—*Resorcin*, and *hydroquinone*, the latter of which is formed by the dry distillation of quinic acid. Hydroquinone, on oxidation, yields quinone,  $C_6H_4O_2$ , and water.

SALICYLIC ALCOHOL (Saligenin),  $C_7H_8O_2 = C_7H_6 \begin{smallmatrix} OH \\ OH \end{smallmatrix}$  is obtained when salicin is heated with dilute sulphuric acid, or exposed to the action of certain ferments—



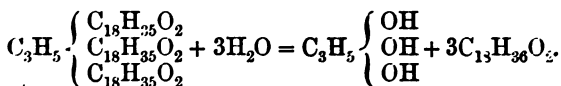
Saligenin crystallizes in colourless scales, which melt at  $82^\circ$ . By oxidation it is converted into salicylic aldehyde.

•  $C_nH_{2n-1}(OH)_3$  GROUP OF ALCOHOLS (TRIHYDRIC)

Two members of this series are known, ordinary glycerine,  $C_3H_5(OH)_3$ , and amyglycerine,  $C_4H_7(OH)_3$ .

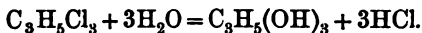
GLYCERIN,  $C_3H_5 \begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix}$ , is a constituent of most animal

and vegetable fats and fixed oils, which are usually mixtures of ethereal salts, formed from glycerine and acids of the oleic and acetic series, and are thus triatomic ethers of the higher fatty acids: thus, mutton and beef fat are composed principally of stearin, or stearic glyceride, which may be regarded as glycerine, in which the three hydroxyl molecules are replaced by three molecules of stearic acid,  $C_{18}H_{35}O_2$ . Palm oil is principally palmitin, or palmitic glyceride, while olive oil is olein, or oleic glyceride. All these glycerides are decomposed by heating with water, yielding glycerine and the corresponding acid, thus—

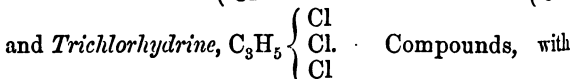
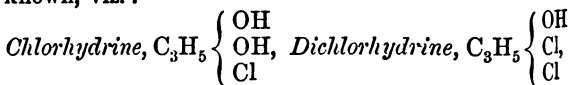


Glycerine is also formed in small quantity in the fermentation of sugar. Glycerine is obtained in large quantities as a bye product in the saponification of fats and oils in the manufacture of soaps. The oil, or fat, is heated with caustic potash, or soda, when a salt of the fatty acid (soap) is formed and glycerine liberated. By adding salt, the soap separates from the solution, and rises to the surface, the glycerine remaining behind; by distilling this spent lye, as it is termed, in a current of superheated steam, the glycerine distils over, together with water, which is subsequently removed by evaporation. The decomposition of glycerides is also effected commercially by heating them with superheated steam, when a mixture of glycerine and free fatty acid distils

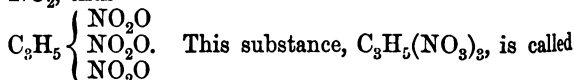
over; an equation representing this decomposition has already been given. Glycerine has been prepared synthetically by heating trichlorhydrine with water in a sealed tube to  $170^{\circ}$ .



Pure glycerine is a colourless syrupy liquid, of specific gravity 1.28, soluble in all proportions in water, and possessing a very sweet taste (from which characteristic it derives its name). It cannot be distilled at the ordinary atmospheric pressure without undergoing decomposition, but may be distilled without change, either under a reduced pressure, or in an atmosphere of steam. Glycerine forms, when heated with hydrochloric acid, compounds called chlorhydrins, in which the hydroxyl group (OH) is replaced by chlorine, water being also formed. Three of these compounds are known, viz. :—



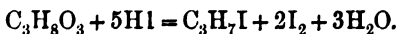
bromine, are also known. When subjected to the action of dilute nitric acid, glycerine forms glycerinic acid,  $\text{C}_3\text{H}_5\text{O}_4$ , by the substitution of an atom of oxygen for two of hydrogen. With concentrated nitric acid a substitution nitrogen product is formed, in which three hydrogen atoms are replaced by the group  $\text{NO}_2$ , thus—



*Trinitrine*, or *Nitroglycerine*. It is a light yellow liquid, of specific gravity 1.6, and possessing violently explosive properties. It is used for blasting purposes, under the name of Nobel's blasting oil, and absorbed

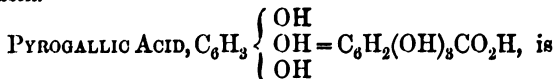
by certain porous substances, and mixed with other ingredients, constitutes the *dynamite* and *lithofracteur* used exclusively for blasting.

When subjected to heat at the ordinary pressure of the air, either alone or mixed with dehydrating agents, glycerine forms acrolein,  $C_3H_8O_3 = 2H_2O + C_3H_4O$  (acrolein). This substance is characterised by its intensely irritating and acrid odour. By the action of hydriodic acid glycerine is reduced to secondary propyl iodide—



#### $C_{11}H_{2n-9}(OH)_3$ GROUP OF ALCOHOLS (TRIHYDRIC)

Of this series only two members are known, viz. :—pyrogallol, or pyrogallic acid, and an isomeride phloroglucin.



obtained by the dry distillation of gallic acid—



It crystallises in long white silky prisms, which melt at  $115^\circ$ . The aqueous solution rapidly absorbs oxygen from the air, especially in presence of an alkali, becoming of a deep-brown colour. Phloroglucin is obtained by fusing catechin, and many other substances, with caustic potash.

#### $C_{11}H_{2n-2}(OH)_4$ GROUP OF ALCOHOLS (TETRAHYDRIC)

One member only of this series is known, viz. :—

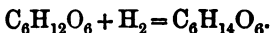
ERYTHRITE,  $C_4H_6(OH)_4$ , which may be obtained from any of the varieties of "*Rocella tinctoria*," by boiling with excess of lime or baryta. It forms large colourless crystals, soluble in water.



### $C_nH_{2n-4}(OH)_6$ SERIES OF ALCOHOLS (HEXAHYDRIC)

Two natural sugars, viz., mannite and dulcite, belong to this series.

MANNITE,  $C_6H_8(OH)_6$ , forms the principal part of *manna*, the dried sap of *Fraxinus ornus*. Mannite may be prepared artificially from certain varieties of sugar by the action of nascent hydrogen, evolved from sodium amalgam and water—



Mannite, on the other hand, may by oxidation be converted into the fermentable sugar,  $C_6H_{12}O_6$ . By further oxidation, mannite may be converted into mannitic acid,  $C_6H_{12}O_7$ , and saccharic acid,  $C_6H_{10}O_8$ . Mannite is regarded as a hexhydric alcohol, by reason of the fact that its six typical hydrogen atoms may be replaced by  $NO_2$ , and that it is attacked by hydriodic acid in the same way as glycerine, iso-hexyl-iodide being formed.

DULCITE (dulcose),  $C_6H_8(OH)_6$ , has been produced artificially by the action of nascent hydrogen on inverted milk sugar. It resembles mannite in its properties.

### CARBOHYDRATES

The carbohydrates are a class of substances which are very widely diffused through the vegetable kingdom, and many of which may be regarded as closely allied to the hexhydric alcohols; the group includes sugars, starches, gums, cellulose, etc., and the members are termed carbohydrates, from the fact of their containing carbon in union with oxygen and hydrogen in the proportion to form water. They may be divided into three classes, viz., the *glucoses*,  $C_6H_{12}O_6$ , the *sucroses*,  $C_{12}H_{22}O_{11}$ , and the *amyloses* or *amylaceous bodies*, ( $C_6H_{10}O_5$ ), which include such substances as starch

and woody fibre. As examples of the glucoses may be taken ordinary grape sugar or dextrose, and fruit sugar or levulose, which differ in turning the plane of polarisation, the former to the right and the latter to the left. Sucrose, or ordinary cane sugar, may be taken as an example of the next group, while starch is a representative of the amyloses.

FIRST GROUP. — *Dextrose*, *Glucose*, (grape sugar),  $C_6H_{12}O_6$ , constitutes the sugar of fruits, and forms the crystalline portion of honey, in which it is mixed with levulose; it is also found in small quantity in the blood, in white of egg, and in healthy urine. In the disease known as diabetes mellitus a large quantity of grape sugar occurs in the urine. Dextrose may be formed by the action of malt on starch, by boiling starch or dextrine with dilute acids, and by the action of acids on several glucosides. It is also a product of the action of dilute acids on sucrose, in which case it is accompanied by levulose. Dextrose may be conveniently prepared by boiling starch with dilute sulphuric acid; the acid liquid is subsequently neutralized by the addition of chalk, and the solution of sugar concentrated by evaporation. It crystallises in cauliflower-like masses, having the composition  $C_6H_{12}O_6 \cdot H_2O$ . It is soluble in its own weight of water, and also dissolves in dilute alcohol. Dextrose does not possess such sweetening power as ordinary cane sugar. In solution it reduces silver from its salts, and precipitates cuprous oxide from alkaline solutions of cupric salts. By the action of nitric acid grape sugar is converted into saccharic acid. Glucose is directly fermentable, and is dextro-rotatory in its action on polarised light. *Levulose*, or left-handed glucose, accompanies dextrose in honey and the juice of ripe fruits, and is produced together with dextrose on boiling a solution of cane sugar with dilute acids; it forms a colourless uncrystallisable syrup, and is more soluble in water and alcohol than dextrose.

Like the last named substance it reduces cupric salts.

**SECOND GROUP.**—*Sucrose* or *Cane Sugar*,  $C_{12}H_{22}O_{11}$ , occurs in the juice of certain plants, the chief of which are the sugar-cane, the beet-root, and the sugar maple; it also occurs to a smaller extent in conjunction with dextrose and levulose in honey and in ripe fruits. Most of the sucrose of commerce is obtained from the sugar cane, although large quantities of beet sugar are prepared in France. The sugar cane contains about 18 per cent. of sugar. The juice is obtained by crushing the cane between rollers; to the liquid thus obtained a small quantity of lime is added, and the whole is raised to the boiling point. The lime precipitates the albuminous substances present, which rise to the surface of the boiling liquid as a scum, which is then removed. The clear liquid is then concentrated in copper pans, filtered, and evaporated to a syrup, which on cooling deposits crystals of brown sugar. The dark coloured mother liquid remaining behind constitutes the molasses or treacle of commerce. Brown sugar is refined and converted into loaf sugar by solution in water, boiling with lime, and finally filtering through thick beds of animal charcoal; the colourless liquid thus procured is concentrated by evaporation in vacuum pans to the crystallising point. Pure sucrose crystallises in monoclinic prisms, which are soluble in one third of their weight of cold water, but are nearly insoluble in alcohol. The specific gravity of sucrose is 1.60, it melts at  $160^{\circ}$  to a colourless liquid, which, when more strongly heated, gives off water, and leaves a dark-coloured mass called caramel. By treatment with strong sulphuric acid sucrose is entirely decomposed with separation of carbon, a reaction which distinguishes it at once from glucose, which, under like conditions, is not so affected. A further distinction is the action on an alkaline solution of a cupric salt, which suffers very little reduction when

boiled with sucrose. Cane sugar forms definite compounds with many metallic salts. It yields saccharic acid on oxidation. Cane sugar is not directly fermentable, suffering under action of ferments a conversion into grape sugar, which then undergoes the vinous fermentation.

*Maltose* is another sugar belonging to this group. It is the final product of the action of diastase on starch. It differs from sucrose in reducing copper solution, but yields, weight for weight, only about two thirds as much cuprous oxide as glucose.

*Lactose* or *Milk Sugar*,  $C_{12}H_{22}O_{11}$ , is found in the milk of the mammalia. It may be obtained by evaporating whey. Lactose is far less soluble in water than sucrose, and also possesses less sweetening power. It is dextro-rotatory in its action on polarised light, and reduces alkaline copper solutions, but produces, weight for weight, slightly less cuprous oxide than glucose. By oxidation it yields mucic and saccharic acids. Lactose like sucrose is not directly fermentable, only entering into fermentation after its solution has remained for some time in contact with yeast. By the action of dilute acids, lactose is converted into a variety of glucose called galactose, which is directly fermentable. When a solution of lactose is allowed to remain for some time in contact with decaying cheese, *lactic acid* is formed in considerable quantity.

The solution of copper, which is reduced by some of the sugars, is produced as follows. A clear solution of cupric sulphate is prepared, and in another vessel a solution is made by dissolving caustic potash and Rochelle salt (double tartrate of potash and soda) in distilled water. On mixing the last named solution with the solution of copper, a clear deep blue liquid is obtained. When a little of this liquid is boiled with glucose, or with any of the sugars capable of acting on it, cuprous oxide is deposited as a dark-red or yellowish powder. If this precipitate is collected

on a weighed filter, washed, and weighed, the amount of glucose present may be ascertained. 100 parts of cuprous oxide represent 50.4 parts of glucose. By boiling starches, and also sugars which do not reduce copper solution, for some time with dilute acid, they suffer conversion into glucose, which may then be estimated in the way indicated.

[TABLE

The following Table shows the Leading Characteristics of the chief varieties of Sugar:—

NAME	ACTION ON POLARISED LIGHT	LEADING CHARACTERISTICS
Mannite, $C_6H_8(OH)_6$ Dulcite or Dulcose, $C_6H_8(OH)_6$	No action	Not directly fermentable; not very sweet; crystalline; is converted by oxidation into <i>Mannitic</i> and <i>Saccharic</i> acids; does not reduce copper solution; freely soluble in water and alcohol. Resembles mannite in its properties, but crystallises in a different form, and yields <i>Mucic</i> acid on oxidation with nitric acid.
Dextrose, Glucose or Grape Sugar, $C_6H_{12}O_6$	Dextro-rotatory	Directly fermentable; less sweet than ordinary cane sugar; imperfectly crystalline; freely soluble in water and dilute alcohol; reduces copper solution; yields <i>Saccharic</i> acid on oxidation; is not blackened by the action of cold concentrated sulphuric acid, with which it unites to form sulpho-saccharic acid.
Levulose, $C_6H_{12}O_6$ Sucrose or Cane Sugar, $C_{12}H_{22}O_{11}$	Laevo-rotatory  Dextro-rotatory	Resembles glucose in its properties, but is not crystallisable; sweeter and more soluble in alcohol. Not directly fermentable; very sweet; crystalline; freely soluble in water, but sparingly so in alcohol; does not reduce copper solution; yields saccharic acid on oxidation, and is blackened and decomposed by the action of cold concentrated sulphuric acid.
Maltose, $C_{12}H_{22}O_{11}$ Lactose or Milk Sugar, $C_{12}H_{22}O_{11}$	Dextro-rotatory  Dextro-rotatory	Crystallisable, and reduces copper salts, but only produces weight for weight two thirds as much cuprous oxide as glucose. Not directly fermentable; not very soluble in water, and not very sweet; crystalline; reduces copper solution, but produces weight for weight slightly less cuprous oxide than glucose; yields mucic and saccharic acids on oxidation.

**THIRD GROUP.—THE AMYLOSES.**—This group, which includes gums and starches, embraces a large number of substances, of which the following are the most important:—

**DEXTRINE**,  $C_6H_{10}O_5$ , is prepared by boiling starch for a short time with dilute acids, and also in conjunction with dextrose, by the action of malt upon starch. It is prepared on a large scale for commercial use, under the title of "British Gum," by heating starch to  $150^\circ$ , either by itself, or with the addition of a small quantity of nitric or hydrochloric acid, which greatly expedites the transformation. Dextrine is very soluble in water, but insoluble in alcohol. It turns the plane of polarisation powerfully to the right. It is converted into *maltose* by the action of malt, and into *dextrose* by boiling with dilute acids.

**GUM ARABIC** is a natural gum which exudes from several species of acacia. It chiefly consists of *arabic acid*,  $C_{12}H_{20}O_{10}$ , united to calcium and potassium. By boiling gum arabic with dilute acid, *arabinose*,  $C_6H_{12}O_6$ , is formed isomeric with dextrose.

**INULIN**,  $n(C_6H_{10}O_5)$ , occurs in the roots of many plants, among which may be mentioned the dahlia. It is intermediate between gum and starch, and yields *lævulose* by prolonged boiling with dilute acids.

**GLYCOGEN**,  $n(C_6H_{10}O_5)$ , is sometimes called *animal starch*, from the fact of its occurrence in the liver of various animals. It is an insoluble powder, which is converted into dextrose by boiling with dilute acids.

**STARCH**,  $n(C_6H_{10}O_5)$ , is a very widely diffused natural vegetable product, occurring more or less in all plants, and forming a large constituent of grain, and of some tuberous roots, such, for instance, as the potato. Starch is a distinctly organised structure, and when viewed under the microscope, is seen to consist of granules of various sizes. The starch granules from different plants vary, both in form and size, to a sufficient extent to render the identification of many

kinds quite possible with the aid of the microscope. The following shows the greatest diameter of the granules of a few of the better known starches :—

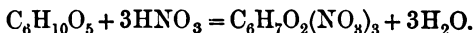
		Millimetres			Millimetres
Potato	-	0.180	Maize	-	0.030
Wheat	-	0.050	Sago	-	0.070

Starch is a white shining powder, soft to the touch ; it is insoluble in cold water, alcohol, or ether. When starch is treated with water at a higher temperature than 70°, the granules swell up, split open, and form a thick paste. If this paste is diluted and boiled for some time, the solution becomes clear, and then contains a soluble form of starch, which may be precipitated by the addition of alcohol. Both soluble and insoluble starch give a deep blue compound with free iodine, the colour of which disappears at a temperature of 100°, and reappears on cooling. When starch is heated to 160° it is converted into dextrine ; dilute sulphuric acid converts it first into a mixture of dextrine and dextrose, and, finally, into dextrose. The diastase of malt acts in a similar way. Strong sulphuric acid dissolves starch, forming an acid compound, while strong nitric acid gives a nitro-substitution product called *xyloidin*,  $C_{12}H_{19}(NO_2)O_{10}$ .

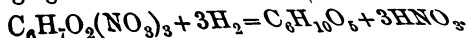
CELLULOSE,  $n(C_6H_{10}O_5)$ , also called *lignin*, is the chief constituent of the structure of plants, forming the various descriptions of woody fibre and cell growth. It exists in an almost pure condition as cotton wool. Pure cellulose is a white substance, insoluble in water and all ordinary solvents, but dissolving in an ammoniacal solution of cupric oxide, from which it may be precipitated in white flocks by the addition of an acid. Iodine does not colour cellulose. Cold concentrated sulphuric acid converts it into a jelly-like substance, which subsequently dissolves ; by diluting this liquid and boiling for some time, replacing the water as it evaporates, the cellulose is eventually entirely



converted into dextrose. Cellulose is acted upon by ordinary nitric acid, being oxidised to oxalic acid. With a mixture of strong sulphuric and nitric acid, cellulose is converted into remarkable nitro-substitution products, in which some of the groups of HO are replaced by a corresponding number of the groups ( $\text{NO}_2$ ). Ordinary *gun cotton*, or *pyroxylin*, is *trinitro-cellulose* or *cellulo-trinitrin*. This is prepared by introducing cotton wool, in small quantities at a time, into a mixture of one volume of nitric acid, specific gravity 1.5, with three volumes of strong sulphuric acid. After the lapse of some hours, the cotton is removed from the acid mixture, thoroughly washed and dried by steam. The product exactly resembles the original cotton in appearance, with the exception of the fibre feeling harsher to the touch. It weighs heavier than the original cotton, and has acquired explosive properties. The following equation shows the action of the nitric acid—



The constitution of pyroxylin may be written either  $\text{C}_6\text{H}_7\text{O}_2(\text{NO}_2)_3$ , if it is regarded as produced from cellulose by the replacement of  $\text{NO}_2$  for HO, or  $\text{C}_6\text{H}_7(\text{NO}_2)_3\text{O}_5$ , if regarded as formed by the substitution of the  $\text{NO}_2$  group for hydrogen. Pyroxylin is insoluble in water, alcohol, or ether, but a special description may be prepared, which is soluble in a mixture of alcohol and ether. This variety is a lower nitration product prepared by treating cotton wool with a weaker acid mixture. The solution of this compound, in a mixture of alcohol and ether, is called *collodion*. It is used for surgical purposes, and for coating the glass plates used for taking photographic negatives. All the nitration products of cellulose are denitrated and converted into ordinary cellulose by the action of reducing agents—



PECTIN is the substance which imparts the power of gelatinising to the boiled juice of ripe fruits. The unripe fruits contain an insoluble substance, pectose, which, during the ripening process, is converted into soluble pectin. The actual composition of pectose and pectin has not been satisfactorily established.

### FERMENTATION

The name *fermentation* has been given to a peculiar class of decompositions, which differ from ordinary chemical changes in being apparently caused by the action of organised bodies, which are low forms of life. The sugars are the principal class of bodies which are subject to this peculiar form of decomposition, and the substances which cause fermentation are known as "ferments." Ferments are of different kinds, and ordinary beer yeast may be taken as a good example. It is a vegetable growth called "*torula cerevisiæ*," or *mycoderma cerevisiæ*, consisting of round or ovoid cells, which increase rapidly when placed in a dilute solution of any of the glucoses, the sugar being decomposed into alcohol and carbonic acid, with small quantities of other products, among which may be mentioned mannite, succinic acid, and glycerine; a further portion of the glucose apparently disappears in furnishing food for the yeast. The following is an enumeration of the different kinds of fermentation:—The alcoholic, the chief products being alcohol and carbonic acid; the acetous, producing acetic acid; the lactic, yielding chiefly lactic acid; the butyric, affording mainly butyric acid; and, finally, the mucous, which gives rise to gum and mannite. As far as is known, most of the ferments which give rise to these special fermentations consist of vegetable growths. The alcoholic fermentation, which is the most important, will not take place under all conditions. If any other forms of sugar than one of the glucosides be present,

they are first changed into glucosides before fermentation can occur. In addition, the sugar solution must not be too strong, and the temperature neither too high nor too low, from 20° to 40° being the most favourable; at 0° fermentation is entirely stopped. Yeast also requires ammoniacal salts and phosphates for its active growth, these substances being generally present in the fermented material. The spontaneous fermentation which often occurs in solutions of some organic substances, is caused by the deposition of fermentative germs from the surrounding air, for if care is taken to preserve the purity of the air which reaches the solution, either by filtration through cotton wool, which arrests the germs, or by passage through a red-hot tube, which destroys them, fermentation does not occur, and organic liquids may be preserved for long periods of time without change.

Besides the peculiar changes caused by the growth and multiplication of *organised living ferments*, there also exists a class of decomposition, brought about by certain substances which act the part of ferments, but which are not organised, and are apparently simply organic compounds. Thus *emulsin*, which is found in bitter almonds, has the power of decomposing amygdalin, and giving rise to hydrocyanic acid, glucose, and benzoic aldehyde. In the same way *myrosin*, which is found in mustard seed, has the property of converting potassium myronate (which also occurs in the seed), into allyl sulphocyanate, glucose, and potassium hydrogen sulphate. Similar reactions are met with in the *ptyalin* of saliva, and the *diastase* of malt, both of which have the property of converting starch into sugar.

#### THE MERCAPTANS OR THIO-ALCOHOLS

These compounds may be considered to possess a relation to ordinary alcohols, inasmuch as they may be

regarded as having the group (SH) in place of the hydroxyl group (OH), they hold the same relation to ordinary alcohols as metallic hydrates do to metallic sulphhydrates—

Ethyl alcohol (or hydrate)  $C_2H_5OH$ .

Sodium hydrate  $NaOH$ .

Ethyl thio-alcohol, or }  $C_2H_5SH$ .  
mercaptan

Sodium sulphhydrate  $NaSH$ .

Mercaptans, corresponding to several members of the monohydric, dihydric, and trihydric alcohols, have been obtained, a general method of formation being by the action of potassium sulphhydrate on haloid derivatives of the hydrocarbons of the  $C_nH_{2n}$  and  $C_nH_{2n+2}$  series. The only member of the thio-alcohols which will be noticed here, is ordinary mercaptan, the thio-alcohol of ethyl.

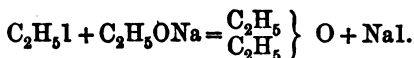
ETHYL THIO-ALCOHOL, MERCAPTAN, ETHYL SULPHYDRATE,  $\left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} S$ , may be obtained by acting on ethyl chloride with potassium sulphhydrate, potassium chloride and ethyl sulphhydrate being formed. Mercaptan is a colourless liquid, which boils at  $36^\circ$ , and possesses the peculiar garlic-like odour characteristic of organic sulphur compounds. Like an ordinary alcohol, mercaptan can exchange its typical hydrogen for metals.

## ETHERS

These compounds may be conveniently regarded as oxides of radicals, of which the corresponding alcohols are the hydrates, and as bearing the same relation to the alcohols that the metallic oxides do to the metallic hydrates, thus:—

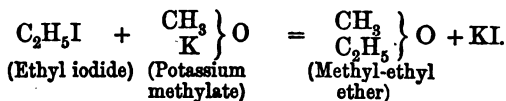
Ethyl hydrate,	$\left. \begin{matrix} C_2H_5 \\ H \end{matrix} \right\} O$	Ethyl oxide,	$\left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\} O$
or alcohol		or ether	
Sodium hydrate	$\left. \begin{matrix} Na \\ H \end{matrix} \right\} O$	Sodium oxide	$\left. \begin{matrix} Na \\ Na \end{matrix} \right\} O$

The ethers corresponding to the members of the ethyl, allyl, and benzyl series of monohydric alcohols, are obtained by acting on the monohaloid derivatives of the corresponding hydrocarbons, with the sodium or potassium derivatives of the corresponding alcohols, thus—



The ethers of the ethyl and allyl series may also be prepared by acting on the acid ethereal salt with the corresponding alcohols.

Besides the *simple ethers*, a series of *compound ethers* are known, viz., ethers containing two different radicals. These may be formed by acting on the monohaloid derivative of one hydrocarbon, with the potassium or sodium derivative of another hydrocarbon, thus—



The following lists give some of the more important simple and compound ethers :—

Simple Ethers		Boiling Point
Di-methyl ether, $\text{C}_2\text{H}_6\text{O} =$	$\left. \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \right\} \text{O}$	- 21°
Di-ethyl ether, $\text{C}_4\text{H}_{10}\text{O} =$	$\left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix} \right\} \text{O}$	35°
Di-butyl ether, $\text{C}_8\text{H}_{18}\text{O} =$	$\left. \begin{matrix} \text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 \end{matrix} \right\} \text{O}$	104°
Di-amyl ether, $\text{C}_{10}\text{H}_{22}\text{O} =$	$\left. \begin{matrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{matrix} \right\} \text{O}$	176°

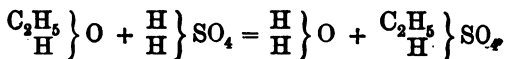
Compound Ethers		Boiling Point
Methyl-ethyl ether, $C_3H_8O = \left. \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \right\} O$		12°
Methyl-amyl ether, $C_6H_{14}O = \left. \begin{matrix} CH_3 \\ C_5H_{11} \end{matrix} \right\} O$		92°
Ethyl-butyl ether, $C_6H_{14}O = \left. \begin{matrix} C_2H_5 \\ C_4H_9 \end{matrix} \right\} O$		80°
Ethyl-amyl ether, $C_7H_{16}O = \left. \begin{matrix} C_2H_5 \\ C_5H_{11} \end{matrix} \right\} O$		112°
Ethyl-hexyl ether, $C_8H_{18}O = \left. \begin{matrix} C_2H_5 \\ C_6H_{13} \end{matrix} \right\} O$		132°

### Simple Ethers

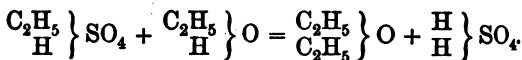
**METHYL ETHER** (di-methyl ether), **METHYL OXIDE**,  $\left. \begin{matrix} CH_3 \\ CH_3 \end{matrix} \right\} O$ , may be prepared by heating methyl alcohol with sulphuric acid. The action which occurs is similar to that which takes place in the preparation of the next member, viz., ethyl ether. Methyl ether is a colourless sweet smelling gas, which may be condensed at  $-21^\circ$  to a colourless liquid.

**DI-ETHYL ETHER**, **ETHYL-OXIDE** (Ordinary Ether),  $\left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\} O$ . This substance is the ordinary well known ether. It may be prepared by acting on ethyl iodide with potassium ethylate, potassium iodide and ether being formed. It is, however, more usually prepared by heating ethyl alcohol with sulphuric acid to a temperature of from  $140^\circ$  to  $145^\circ$ . By allowing fresh alcohol to flow into the mixture at such a rate that the temperature remains within the prescribed limits, an almost unlimited amount of alcohol may be converted into ether and water. Two molecules of ethyl alcohol ( $C_2H_5OH$ ) contain the elements of one molecule of ethyl ether and one of water. The transformation of the alcohol into ether is not, however, direct. The first product of the action of the sulphuric

acid on the alcohol is the formation of hydric ethyl sulphate, or sulphovinic acid, thus—



The sulphovinic acid,  $\text{C}_2\text{H}_5 \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\} \text{SO}_4$ , then reacts on unaltered alcohol as follows:—



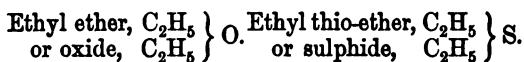
The sulphuric acid thus liberated is free to react on a further portion of alcohol, and so the transformation is continued. This method is called "*the continuous etherification process.*" Ether is a colourless, mobile liquid, having a peculiarly strong and exhilarating odour. It is very volatile, having a boiling point of  $35^\circ$ , and specific gravity of 0.736. Ether is very combustible, and burns with a luminous flame, and its vapour, which is very heavy, forms an explosive mixture with air. Ether is acted on by both bromine and chlorine; with the latter element a series of substitution compounds are formed, the first of which is  $\text{C}_2\text{H}_4\text{Cl} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_4\text{Cl} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$ , and the last,  $\text{C}_2\text{Cl}_5 \left\{ \begin{smallmatrix} \text{C}_2\text{Cl}_5 \\ \text{C}_2\text{Cl}_5 \end{smallmatrix} \right\} \text{O}$ . By oxidation ether yields the same products as its corresponding alcohol.

*Amyl Ether*,  $\text{C}_5\text{H}_{11} \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\} \text{O}$ , is obtained by the action of potassium amylate on amyl iodide. It is a colourless liquid, boiling at  $176^\circ$ .

### *Thio-Ethers*

The thio-ethers contain sulphur in the place of oxygen, and bear the same relation to the ethers that

the metallic sulphides do to the metallic oxides, thus—



The thio-ethers are generally colourless or yellow liquids of offensive odour. The ethyl compound,  $C_2H_5 \left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \end{array} \right\} S$ , is a colourless liquid of strong unpleasant odour, and boiling at  $91^\circ$ . It may be prepared by the action of potassium sulphide on ethyl chloride.

### ALDEHYDES

The aldehydes are the first products of the oxidation of the primary alcohols, and are formed by a withdrawal of hydrogen. They are distinguished from the *Ketones*, which are similarly related to the secondary alcohols, by the fact of their yielding on oxidation acids containing the same number of carbon atoms; thus alcohol,  $C_2H_6O$ , by withdrawal of two atoms of hydrogen, becomes ordinary aldehyde,  $C_2H_4O$ , and by direct addition of oxygen, aldehyde passes into acetic acid,  $C_2H_4O_2$ . The aldehydes are divided into groups corresponding to their relations to the alcohols. It was pointed out in speaking of the alcohols that methyl alcohol might be formulated as  $CH_3.OH$ , while ethyl alcohol might be regarded as  $CH_3.CH_2.OH$ , and the higher alcohols as being represented by the replacement of the group  $CH_3$  by different monad radicals, propyl alcohol being  $(C_2H_5)CH_2.OH$ , and butyl alcohol,  $(C_3H_7)CH_2.OH$ . In the aldehydes the  $CH_2.OH$  is replaced by  $COH$ . Starting with methyl aldehyde,  $H.COH$ , ethyl aldehyde is



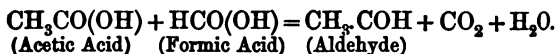
$\text{CH}_3\text{COH}$ , propyl aldehyde,  $\text{C}_2\text{H}_5\text{COH}$ , and butyl aldehyde,  $\text{C}_3\text{H}_7\text{COH}$ .

Of the aldehydes the following are the most important :—

$\text{C}_n\text{H}_{2n+1}\text{COH}$  SERIES—THE ACETIC SERIES OF  
ALDEHYDES

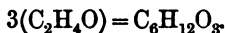
This group includes methyl, ethyl, propyl, butyl, and pentyl aldehydes, the most important member of which is the ethyl compound.

ETHYL, or ACETIC ALDEHYDE,  $\text{C}_2\text{H}_4\text{O} = \text{CH}_3\text{COH}$ , is the first product of the oxidation of ordinary alcohol, no matter by what means such oxidation is accomplished. Aldehyde may be conveniently prepared from a mixture of dilute alcohol with sulphuric acid and manganese dioxide, or potassium bichromate. It may also be prepared by distilling a mixture of calcium acetate and formate—



Aldehyde is a colourless liquid of suffocating odour. It has a specific gravity of .80, boils at  $21^\circ$ , and is soluble in water and alcohol. It is neutral to test paper, but acquires an acid reaction on exposure to air from a partial conversion into acetic acid, which is the final product of its oxidation. A solution of aldehyde warmed with solution of silver nitrate, to which a drop of ammonia has been added, reduces the silver to the metallic state, in the form of a bright mirror on the sides of the vessel. By the action of nascent hydrogen aldehyde is readily converted into *alcohol*; when treated with chlorine it forms *acetyl chloride*,  $\text{CH}_3\text{COCl}$ , and by heating with potassium hydrate solution, *aldehyde resin* is formed. Aldehyde exists in three polymeric modifications; in the pure state it may be preserved in closed vessels without

change, but if a trace of hydrochloric or sulphuric acid be added, and the vessel kept cool by a freezing mixture, crystalline needles of metaldehyde are formed. If, after the addition to ordinary aldehyde of a trace of sulphuric or hydrochloric acid, no precaution is observed to keep the mixture cool, it heats and even boils, and is entirely converted into paraldehyde—



It is a colourless liquid, boiling at  $124^\circ$ . When aldehyde is heated with a little zinc chloride and water in a closed tube, croton aldehyde,  $\text{C}_4\text{H}_6\text{O}$ , and water are formed,  $2\text{C}_2\text{H}_4\text{O} = \text{C}_4\text{H}_6\text{O} + \text{H}_2\text{O}$ .

Aldehyde forms a crystalline compound with ammonia (aldehyde-ammonia)  $\text{CH}_3\cdot\text{COH}(\text{NH}_2)$  which is decomposed by heating with dilute sulphuric acid, aldehyde being liberated.

CHLORAL, TRICHLORALDEHYDE,  $\text{C}_2\text{HCl}_3\text{O} = \text{CCl}_3\cdot\text{COH}$ , may be formed from aldehyde, but is more frequently prepared by the continued action of chlorine upon alcohol. It is a colourless heavy liquid of powerful odour, boiling at  $94^\circ$ , and of specific gravity 1.5. It yields on oxidation trichloroacetic acid, and is therefore regarded as the aldehyde of that body. Chloral much resembles aldehyde in its properties, yielding a crystalline compound with ammonia. On mixing chloral with water much heat is given out, and chloral hydrate,  $\text{CCl}_3\text{CH}(\text{OH})_2$ , produced—a substance extensively used in medicine for producing sleep. When acted upon by alkalis, chloral hydrate yields chloroform and a formate—



It is a similar transformation which gives rise to the soporific effects of chloral hydrate, the change occurring *in the blood of the patient*.

ACETAL,  $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2 = \left. \begin{matrix} \text{C}_2\text{H}_4 \\ (\text{C}_2\text{H}_5)_2 \end{matrix} \right\} \text{O}_2$ , is a derivative of aldehyde, and is obtained by heating a mixture of aldehyde and alcohol. It is a colourless liquid of agreeable odour, boiling at  $104^\circ$ .

DI-METHYL ACETAL,  $\left. \begin{matrix} \text{C}_2\text{H}_4 \\ (\text{CH}_3)_2 \end{matrix} \right\} \text{O}_2$ , is also known.

#### ACRYLIC SERIES OF ALDEHYDES $\text{C}_n\text{H}_{2n-1}\text{COH}$

Two members of this group are known, the chief of which is ACROLEIN or ACRYLIC ALDEHYDE,  $\text{C}_3\text{H}_4\text{O} = \text{CH}_2\text{CH.COH}$ . This body may be formed by the oxidation of allyl alcohol. It is always produced during the destructive distillation of fats containing glycerides. It is best prepared by heating glycerine with a dehydrating agent such as phosphoric oxide—



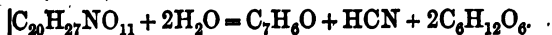
Acrolein is a colourless liquid, boiling at  $52^\circ$ , and possessing an odour which is irritating to the nose and eyes. It yields, by moderate oxidation, acrylic acid,  $\text{C}_3\text{H}_4\text{O}_3$ , but under the influence of powerful oxidising agents, it yields formic acid, carbonic anhydride, and water. Acrolein is converted into allyl alcohol by the action of nascent hydrogen.

#### BENZOIC SERIES OF ALDEHYDES $\text{C}_n\text{H}_{2n-7}\text{COH}$

The principal members of this series are as follow :—

BENZOIC ALDEHYDE.—Bitter almond oil,  $\text{C}_7\text{H}_6\text{O} = \text{C}_6\text{H}_5\text{COH}$ , may be produced by the oxidation of benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2(\text{OH})$ . It may also be formed by distilling a mixture of a benzoate and a formate. Benzoic aldehyde is generally prepared from bitter almonds, which contain amygdalin,  $\text{C}_{20}\text{H}_{27}\text{NO}_{11} + 3\text{H}_2\text{O}$ . By the action of synaptase, also contained in the seed, the

amygdalin is decomposed into bitter almond oil, hydrocyanic acid, and glucose—



Benzoic aldehyde is a colourless liquid, of specific gravity 1.06. It rapidly absorbs oxygen from the air, and becomes converted into crystalline benzoic acid. The vapour of benzoic aldehyde is decomposed by passage through a red-hot tube, benzol and carbon monoxide being formed, and by the action of chlorine benzoic chloride,  $C_6H_5.COCl$ , is formed.

CUMIC ALDEHYDE,  $C_6H_4(C_8H_7)COH$ , exists in oil of cumin. It closely resembles benzoic acid in its reactions.

SALICYLIC ALDEHYDE.—*Salicylol*,  $C_6H_4(OH).COH$ , exists ready formed in the flowers of the *Spiræa Ulmaria*, or Meadow Sweet. It may be produced by the oxidation of the corresponding alcohol, Saligenin,  $C_7H_8O_2$ , a product derived from salicin, the bitter principle of willow bark. Salicylol forms salicylic acid on oxidation, and dissolves in caustic alkalis to form metallic derivatives. The sodium compound,  $C_6H_4(ONa)COH$ , when treated with acetic anhydride, yields *Cumarin*,  $C_9H_6O_2$ , a crystalline solid which is the odoriferous principle of the Tonka bean, of Sweet Woodruff, and of certain sweet scented grasses.

ANISIC ALDEHYDE,  $C_8H_8O_2 = C_6H_4(OCH_3)COH$ , is formed on the oxidation of anise oil (anise alcohol). It closely resembles benzoic and salicylic aldehydes in its chemical behaviour.

### $C_nH_{2n-9}COH$ SERIES OF ALDEHYDES

CINNAMIC ALDEHYDE,  $C_9H_8O = CH(C_6H_5)CH.CO$ , is the chief constituent of oil of cassia or cinnamon. It yields cinnamic acid,  $C_9H_7O_2$ , on oxidation.

## ACIDS

The organic acids may be regarded as formed from the corresponding primary alcohols by the conversion of the  $\text{CH}_2\text{OH}$  group into the *carboxyl* group,  $\text{CO.OH}$ . The organic acids have the power of decomposing metallic carbonates to form salts, in which the hydrogen of the acid is replaced by metal, and the basicity of the respective acids has been found to be in direct ratio to the number of  $\text{CO.OH}$  groups contained in their formulæ. A large number of acids are known; they may be regarded as derived from the isologous series of hydrocarbons by the replacement of one or more atoms of hydrogen by a corresponding number of carboxyl groups.

The following is a list of the more important members of the first or acetic series of monobasic acids ( $\text{C}_n\text{H}_{2n+1}\text{CO(OH)}$ ), together with the hydrocarbons from which they are derived. They differ from the corresponding hydrocarbons, in containing two equivalents less hydrogen, and, in addition, two equivalents of oxygen:—

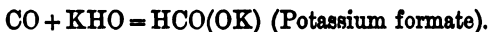
Hydrocarbon	Acid	
Methyl, $\text{CH}_4$	Formic acid,	$\text{CH}_2\text{O}_2 = \text{HCO(OH)}$
Ethyl, $\text{C}_2\text{H}_6$	Acetic acid,	$\text{C}_2\text{H}_4\text{O}_2 = \text{CH}_3\text{CO(OH)}$
Propyl, $\text{C}_3\text{H}_8$	Propionic acid,	$\text{C}_3\text{H}_6\text{O}_2 = \text{C}_2\text{H}_5\text{CO(OH)}$
Butyl, $\text{C}_4\text{H}_{10}$	Butyric,	$\text{C}_4\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7\text{CO(OH)}$
Pentyl, $\text{C}_5\text{H}_{12}$	Valeric,	$\text{C}_5\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_9\text{CO(OH)}$
Hexyl, $\text{C}_6\text{H}_{14}$	Caproic,	$\text{C}_6\text{H}_{12}\text{O}_2 = \text{C}_5\text{H}_{11}\text{CO(OH)}$
Heptyl, $\text{C}_7\text{H}_{16}$	Enanthylic,	$\text{C}_7\text{H}_{14}\text{O}_2 = \text{C}_6\text{H}_{13}\text{CO(OH)}$
Ocetyl, $\text{C}_8\text{H}_{18}$	Caprylic,	$\text{C}_8\text{H}_{16}\text{O}_2 = \text{C}_7\text{H}_{15}\text{CO(OH)}$
Nonyl, $\text{C}_9\text{H}_{20}$	Pelargonic,	$\text{C}_9\text{H}_{18}\text{O}_2 = \text{C}_8\text{H}_{17}\text{CO(OH)}$

This series also includes the following acids:—

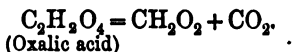
Palmitic acid,	$\text{C}_{15}\text{H}_{31}\text{CO(OH)}$
Stearic acid,	$\text{C}_{17}\text{H}_{35}\text{CO(OH)}$
Cerotic acid,	$\text{C}_{25}\text{H}_{51}\text{CO(OH)}$

The primary monobasic acids of this series are formed by the oxidation of the corresponding alcohols, or aldehydes; other methods of preparation are used in special cases.

FORMIC ACID,  $\text{CH}_2\text{O}_2 = \text{HCO}(\text{OH})$ , derives its name from its occurrence in the bodies of red ants. It is also found in stinging nettles. It has been produced in small quantity by passing the electric current through a mixture of carbonic anhydride and hydrogen,  $\text{CO}_2 + \text{H}_2 = \text{CH}_2\text{O}_2$ . It has also been formed by the action of carbonic oxide on potash at a temperature of  $100^\circ$ —



Formic acid may be directly produced by the oxidation of methyl alcohol, but is more conveniently prepared by distilling a mixture of oxalic acid and glycerine, with the addition of a little water—

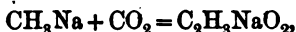


To obtain the acid free from water, lead formate must be first formed, and subsequently decomposed by a current of sulphuretted hydrogen. Formic acid is a highly corrosive, colourless, inflammable liquid, of specific gravity 1.23, possessing a penetrating odour, and boiling at  $100^\circ$ . It is miscible in all proportions with water. When heated with sulphuric acid, it is decomposed into carbonic acid and water. A formate heated with excess of baryta yields an oxalate—



Formic acid is monobasic, and forms a well-defined series of salts, which are soluble in water. It is a powerful reducing agent.

**Acetic Acid**,  $C_2H_4O_2 = CH_3CO(OH)$ .—This acid is present in small quantity in the juices of many plants, and has been known in the dilute state of vinegar from a very early period; it may be produced by the direct combination of carbon dioxide and sodium methyl—

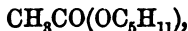


also by bringing a mixture of acetylene and oxygen in contact with a solution of potash—



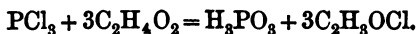
Acetic acid is produced on a large scale from the destructive distillation of wood, the crude acid thus obtained being called pyroligneous acid. In preparing pure acetic acid from this crude product, the acid liquid is neutralised by the addition of lime, the solution of calcium acetate concentrated by evaporation, and mixed with a solution of sodium sulphate. Mutual decomposition of the two salts then takes place, by which insoluble calcium sulphate is precipitated, and soluble sodium acetate remains in solution. The solution is then filtered, evaporated, and the sodium acetate which crystallises out, drained from the dark "mother liquor." The salt is then cautiously heated to expel water of crystallisation, and then gently fused, by which all traces of tarry matter are expelled or decomposed. The dry salt is then dissolved in water, and purified by re-crystallisation, and may then be made to yield pure acetic acid by distillation with sulphuric acid. Vinegar is prepared in large quantities by the oxidation of weak alcoholic liquids, either through the agency of the acetous fermentation, or by a more rapid process, by which the liquid is made to flow slowly through vessels filled with basket work, up which a current of air is passing. Pure acetic acid is a colourless and highly corrosive liquid, having a pungent odour; it has a specific gravity of 1.063, boils at  $119^\circ$ , and solidifies at  $17^\circ$  to a white, ice-

like mass, a property from which the name of glacial acetic acid is derived. Acetic acid dissolves in water in all proportions, and the dilute liquid, when submitted to distillation, becomes concentrated; a weak acid distilling over, and an acid of specific gravity 1.073 finally remaining in the retort. Acetic acid is monobasic, forming a well-defined series of salts, the acetates of which are mostly soluble. Lead acetate is the ordinary sugar of lead. Verdigris consists of copper acetate, while the acetates of aluminium and iron are used as mordants by dyers and calico printers. Acetic acid forms a series of *ethereal salts*, or compound ethers, by the substitution of the radicals methyl, ethyl, etc., for the atoms of replaceable hydrogen. One of the most remarkable of these compounds is isoamylic acetate—



which possesses the odour of the jargonelle pear, and is used for flavouring purposes. By the action of the halogens, acetic acid yields haloid substitution derivatives.

ACETYL CHLORIDE,  $\text{C}_2\text{H}_3\text{OCl} = \text{CH}_3\text{COCl}$ , is formed by the action of phosphorus tri-chloride on acetic acid—



It is a colourless liquid of pungent odour, boiling at  $55^\circ$ , and decomposed by water into acetic and hydrochloric acids.

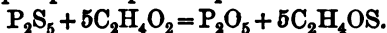
ACETYL OXIDE, ACETIC ANHYDRIDE,  $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{matrix} \right\} \text{O}$ , is a colourless liquid, formed by the action of acetyl chloride on a metallic acetate. It boils at  $138^\circ$ , and by the action of water is converted into acetic acid.

ACETIC PEROXIDE,  $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{matrix} \right\} \text{O}_2$ , is prepared by the action of barium dioxide on acetyl acetate. It is a colourless viscid liquid, which is a powerful oxidising



agent, and decomposes with explosive violence on the application of heat.

THI-ACETIC ACID,  $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{matrix} \right\} \text{S}$ , is obtained by the action of phosphorus pentasulphide on acetic acid—



It bears the same relation to acetic acid as mercaptan does to alcohol. It is a colourless liquid of nauseous odour, boiling at  $93^\circ$ .

PROPIONIC ACID,  $\text{C}_3\text{H}_6\text{O}_2 = \text{C}_2\text{H}_5\text{CO}(\text{OH})$ , resembles acetic acid, and may be produced by heating lactic acid with hydriodic acid. It is a liquid boiling at  $140^\circ$ .

BUTYRIC ACID,  $\text{C}_4\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7\text{CO}(\text{OH})$ , exists in two modifications, viz., normal butyric acid, and isobutyric acid. The normal acid is present in small quantity in butter, in perspiration, and in the juice of human flesh. It is best prepared by fermenting a mixture of sugar, chalk, and cheese. It is a liquid boiling at  $163^\circ$ , and is soluble in water.

VALERIC ACID,  $\text{C}_5\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_9\text{CO}(\text{OH})$ , exists in four isomeric modifications. The normal acid may be obtained by the oxidation of amylic alcohol. Valeric acid boils at  $185^\circ$ .

*Palmitic, stearic, and cerotic acids*, are met with in ordinary fats.

PALMITIC ACID,  $\text{C}_{15}\text{H}_{31}\text{CO}(\text{OH})$ , exists as an ethereal salt in nearly all vegetable fats. Palm oil consists mainly of palmitic glyceride, whilst spermaceti is composed of cetylic palmitate, and by saponifying these substances with caustic alkalis, and subsequently decomposing the compounds by a mineral acid, palmitic acid is obtained as a colourless solid, melting at  $62^\circ$ , and insoluble in water.

STEARIC ACID,  $\text{C}_{17}\text{H}_{35}\text{CO}(\text{OH})$ , occurs in combination with glycerine in most fats, and may be most readily obtained from beef or mutton suet by a method similar to that by which palmitic acid is prepared. Stearic acid closely resembles palmitic acid in its physical properties.

**CEROTIC ACID**,  $C_{26}H_{53}CO(OH)$ , is the main constituent of that portion of common beeswax which is soluble in boiling alcohol. It resembles the two previous acids, and melts at  $78^{\circ}$ .

**THE LACTIC SERIES OF ACIDS** ( $C_nH_{2n}(OH)CO(OH)$ ). This series includes—

Carbonic acid,  $CH_2O_3 = CO(OH)_2$ .

Glycollic acid,  $C_2H_4O_3 = CH_2(OH)CO(OH)$ .

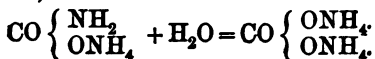
Lactic acid,  $C_3H_6O_3 = CH_3CH(OH)CO(OH)$ .

**CARBONIC ACID**,  $H_2CO_3 = CO(OH)_2$ , is the first member of the lactic series. It is only known in its salts, and is dibasic. Carbonic acid unites with the potassium and sodium derivatives of the alcohols.

**ETHYL CARBONATE**,  $CO(OC_2H_5)_2 = \left. \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \right\} CO_2$ , is obtained by acting on silver carbonate with ethyl iodide. It is a colourless liquid of aromatic odour, boiling at  $126^{\circ}$ . It corresponds to sodium carbonate  $\left. \begin{matrix} Na \\ Na \end{matrix} \right\} CO_3$ .

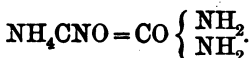
**AMIDES OF CARBONIC ACID.** Carbonic acid yields a normal and an acid amide. The normal amide is carbamide, or urea, while the acid amide is carbamic acid.

**CARBAMIC ACID**,  $CO(NH_2)OH$ , is not known in the free state, but the ammonium salt,  $CO(NH_2)ONH_4$ , is formed on passing a mixture of dry gaseous ammonia and carbon dioxide into anhydrous alcohol. Ammonium carbamate is a white crystalline salt which, on the addition of water, is converted into ammonium carbonate—



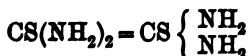
**CARBAMIDE, UREA**,  $CO(NH_2)_2 = CO \left\{ \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right.$  This is a compound which forms the principal solid constituent of human urine, from which fact its name, "Urea," is

derived. It is a product of the oxidation of the nitrogenous constituents of the body, and the amount of excreted urea is therefore a measure of the activity of the changes which are taking place. Urea may be prepared artificially in several ways, viz., by heating ammonium carbonate for some hours in a closed tube to  $135^{\circ}$ , by the action of ammonia on carbon oxychloride (carbonyl chloride), and by heating ammonium cyanate—



The latter process is that by which Woehler first demonstrated the possibility of the artificial production of urea, which had previously been known only as an excretive product of animal life. Urea may be prepared by heating a mixture of yellow prussiate of potash and manganese dioxide, by which potassium cyanate is formed. This salt is dissolved out by water, sulphate of ammonia added, and the whole evaporated to dryness, by which the ammonium cyanate is converted into urea, which may then be dissolved out by alcohol. Urea is very soluble in water, and crystallises in long white prisms. It fuses when heated to  $120^{\circ}$ , and begins to decompose. The proof of urea being an amide of carbonic acid is the fact that, when heated with water in a closed tube to  $100^{\circ}$ , it is resolved into carbonic acid and ammonia. When acted upon by an alkaline solution of a hypochlorite or hypobromite, or by nitrous acid, urea is decomposed into water, carbon dioxide, and free nitrogen. On this reaction, a process of estimating urea has been founded, the measure of gaseous nitrogen obtained being an index of the amount of the substance present. Urea forms compounds with acids, of which the oxalate and nitrate are the most important. It also unites with metallic oxides, such as the mercuric.

## SULPHOCARBAMIDE. SULPHUR UREA—

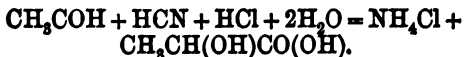


is produced when ammonium sulphocyanide is heated to  $170^\circ$  for two or three hours. It crystallises in white rhombic prisms, and forms compounds with acids.

**COMPOUND UREAS.**—These compounds may be considered as urea, in which one or more of the hydrogen atoms is replaced by an organic radical, such as ethyl, methyl, etc., or by an oxidised radical, such as acetal. They are formed by acting on cyanic acid with a compound ammonia.

**GLYCOLLIC ACID**,  $\text{C}_2\text{H}_4\text{O}_3 = \text{CH}_2(\text{OH})\text{CO}(\text{OH})$ , is obtained from the oxidation of glycol, and is also formed by heating a monohaloid derivative of acetic acid with water, and by the action of nascent hydrogen on oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ). Glycollic acid forms white deliquescent crystals, which melt at  $80^\circ$ ; it is converted by nascent hydrogen into acetic acid, and by oxidising agents into oxalic acid. Glycollic acid is monobasic, and unites with bases to form glycollates.

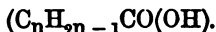
**LACTIC ACID** (Oxypropionic Acid),  $\text{C}_3\text{H}_6\text{O}_3$ , or  $\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH})$ , exists in four isomeric modifications. It is contained in sour milk, its origin being the milk sugar which has undergone a peculiar kind of fermentation (the lactic). It may also be obtained by the oxidation of propyl glycol, and by allowing a mixture of aldehyde, hydrocyanic acid, and hydrochloric acid, to remain in contact for several days.



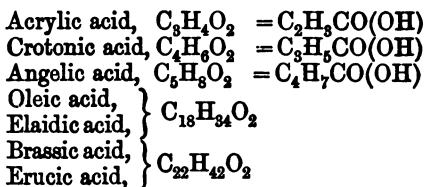
Lactic acid cannot be obtained in the anhydrous state, but in its most concentrated form is a syrupy liquid, of specific gravity 1.215. It decomposes when heated into lactic anhydride, or lactide,  $\text{C}_3\text{H}_4\text{O}_3$ , and dilactic acid,  $\text{C}_6\text{H}_{10}\text{O}_5$ . Lactic acid yields on oxidation acetic

and formic acids, and carbon dioxide. It is reduced to propionic acid by the action of hydriodic acid. Lactic acid forms a well-defined series of salts. A modification of ordinary lactic acid (sarcosylactic acid) is found in the juice of flesh. It consists really of two acids, the paralactic, and the ethene lactic.

ACRYLIC SERIES OF MONOBASIC ACIDS—



The following are the principal members of this series :—



These acids may be formed by the oxidation of the aldehydes of the acrylic series, and by other special methods.

ACRYLIC ACID,  $C_3H_3O \left\{ \begin{array}{l} O \\ H \end{array} \right\}$ , or,  $C_2H_3CO(ON)$ , is formed by the oxidation of acrolein. It is a colourless liquid, boiling at  $140^\circ$ , and resembling acetic acid in its properties. It unites with hydrogen to form *propionic acid*.

CROTONIC ACID,  $C_4H_6O_2$ , is said to occur in croton oil; *Angelica acid*,  $C_5H_8O_2$ , in archangel root. Brassic acid is contained in colza oil; and erucic acid in rape seed oil.

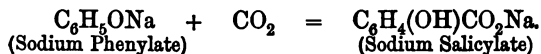
OLEIC ACID,  $C_{18}H_{34}O_2$ , is a liquid which occurs in most natural fats and fixed oils, in combination with glycerine. It is insoluble in water, melts at  $14^\circ$ , oxidises on exposure to air, and by the action of nitric peroxide is converted into an isomeric modification, elaidic acid, which is a solid body, melting at  $42^\circ$ .

THE BENZOIC SERIES OF MONOBASIC ACIDS ( $C_nH_{2n-7}CO(OH)$ ). Of this series the most important member is *Benzoic acid*.

BENZOIC ACID,  $C_7H_6O_2 (= C_6H_5CO(OH))$ , is a constituent of many gums and resins, and is especially abundant in gum benzoin. It also occurs in the urine of cows. It may be formed by the oxidation of benzyl alcohol and bitter almond oil (benzoic aldehyde). Benzoic acid is most easily prepared by submitting gum benzoin to sublimation. As thus prepared, it forms light feathery crystals, possessing a fragrant odour from the presence of traces of volatile oil. Pure benzoic acid is without odour; it fuses at  $121^\circ$ , boils at  $250^\circ$ , and dissolves freely in hot water and in alcohol. Benzoic acid forms a well-defined series of salts, which are mostly soluble; ferric benzoate is, however, insoluble.

OXYBENZOIC, OR SALICYLIC SERIES OF MONOBASIC ACIDS ( $C_nH_{2n-8}(OH)CO(OH)$ ). The most important members of this group are oxybenzoic acid and salicylic acid: they are isomeric.

OXYBENZOIC ACID,  $C_6H_4(OH)CO(OH)$ , is obtained by heating chlorbenzoic acid with caustic potash, while *salicylic acid*, its isomer, is found together with salicylic aldehyde in the flowers of *Spiraea ulmaria*. It may be formed by the oxidation of the aldehyde, or of saligenin (the alcohol), and also by the action of carbon dioxide on the sodium derivative of phenol—

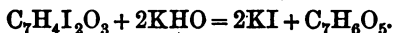


On the other hand, salicylic acid is resolved by heat into phenol and carbon dioxide. The methyl compound of salicylic acid occurs in the oil of winter green (*Gaultheria procumbens*).

GALLIC SERIES OF MONOBASIC ACIDS—

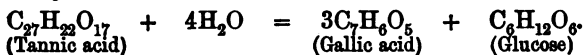


GALLIC ACID (tri-oxybenzoic acid),  $C_7H_6O_5 = C_6H_2(OH)_3CO(OH)$ , has been obtained by the action of caustic potash on di-iodo-salicylic acid—



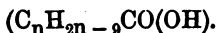
It is, however, best obtained from tannin (see tannic acid). Gallic acid crystallises in white needles. It is soluble in water, and the aqueous solution acquires a deep blue colour when treated with ferric salts, and does not precipitate gelatine; the last named property distinguishes it from tannic acid. When heated gallic acid yields carbon dioxide and pyrogallic acid (a tri-hydric alcohol, sometimes called trihydroxyl benzene). *Tannic acids*, or *tannins*, may be best considered in this group. The tannins, together with salicin and amygdalin, are sometimes termed *glucosides*, from the fact of their yielding glucose among other products on boiling with dilute acid. The tannins are widely diffused through the vegetable kingdom. They generally possess a faintly acid reaction, are amorphous, precipitate gelatine from its solutions, and with ferric salts give a blue, black, or green coloration. Vegetable materials containing tannin, such as aleppo nut galls, oak bark, etc., are much used in the arts for tanning hides, by this means converting them into leather, the property of which, in withstanding atmospheric agencies, is due to the nonputrescent nature of the combination of the tannin with animal gelatins. The black compound formed by tannin with iron salts is also commercially utilised in the manufacture of ink. Aleppo galls, which are excrescences produced by the puncture of an insect on certain species of oak, are very rich in tannin, and this substance may be extracted by treating the powdered galls with ether containing a little water and alcohol. A solution is obtained in two layers, the bottom or aqueous portion containing the tannin, which may be obtained in the solid state by

evaporation in vacuo, over sulphuric acid. Tannin is a yellowish amorphous mass, soluble in water and alcohol, insoluble in pure ether. When exposed for some time in a moist condition to the air, or boiled with dilute acids, tannic acid is converted into *gallic acid* and *glucose*—



Tannin yields pyrogalllic acid when submitted to dry distillation.

CINNAMIC SERIES OF MONOBASIC ACIDS—

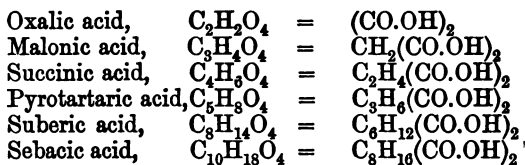


Of this series one member only need be mentioned, viz:—

CINNAMIC ACID,  $\text{C}_8\text{H}_7\text{CO}(\text{OH})$ . This acid exists ready formed in Peru and tolu balsam, and in styrax. It may be obtained by the oxidation of cinnamic aldehyde (cinnamon oil).

#### DIBASIC ACIDS

THE SUCCINIC ACID SERIES  $(\text{C}_n\text{H}_{2n}(\text{COOH})_2)$ . The principal members of this group are the following:—

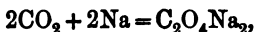


Isomeric modifications of several of the above acids have been obtained. Most of the series are natural products found in the vegetable kingdom. Being dibasic, they yield two series of metallic and ethereal salts.

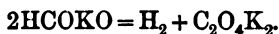
OXALIC ACID,  $\text{C}_2\text{H}_2\text{O}_4$ , is found in the juice of a great many plants, sometimes in the free state, some-



times as a sodium or potassium salt, but more frequently as calcium oxalate. The latter compound is also met with in urine, and urinary deposits. Oxalic acid is a frequent product of the oxidation of many organic substances, which yield it when treated with nitric acid, or fused with caustic potash. Oxalic acid may be produced synthetically by the action of carbon dioxide on sodium at the boiling point of mercury—



and also by heating potassium formate—



Oxalic acid may be more readily prepared by heating sugar with nitric acid, but is manufactured on a large scale by heating sawdust with caustic potash. Potassium oxalate is thus formed, which is dissolved in water, and a calcium salt added, by which a precipitate of calcium oxalate is formed, which, when decomposed with sulphuric acid, yields free oxalic acid. From its aqueous solution, oxalic acid crystallises in colourless prisms, having the composition  $\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$ . The two equivalents of water of crystallisation may be expelled at a temperature of  $100^\circ$ . By exposure to a temperature of  $160^\circ$  it is decomposed, carbon dioxide, carbonic oxide, water, and formic acid being produced, while a little oxalic acid sublimes unchanged. If heated with dehydrating agents, carbon dioxide, carbonic oxide, and water are the products of decomposition, while by powerful oxidising agents oxalic acid is entirely converted into carbon dioxide and water. The salts of oxalic acid are numerous, and are divided into normal oxalates and acid oxalates. Both of the potassium compounds are well marked.

Normal potassium oxalate,  $\text{C}_2\text{K}_2\text{O}_4 + \text{H}_2\text{O}$ .

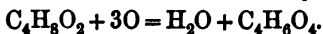
Hydrogen potassium oxalate,  $\text{C}_2\text{KHO}_4 + \text{H}_2\text{O}$ .

A quadroxalate is also known.

The oxalates of the alkali metals are all soluble; those of the other metals are, as a rule, insoluble. The hydrogen in oxalic acid is not only replaceable by a metallic base, but by a hydrocarbon group forming ethereal oxalates; thus ethyl oxalate is  $C_2(C_2H_5)_2O_4$ .

MALONIC ACID,  $C_3H_4O_4$ , is obtained from the oxidation of malic acid. It may also be prepared synthetically by the oxidation of ethene-lactic acid, and by the action of potash on ethyl cyano-acetate.

SUCCINIC ACID,  $C_4H_6O_4$ , exists in amber, in several resins, and, to a small extent, in many animal juices. It can be prepared by fermentation from malic acid, and by subjecting amber to dry distillation. It is also produced by the action of nitric acid on butyric acid—



Succinic acid is also formed by the action of hydriodic acid on malic and tartaric acid.

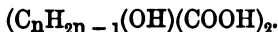
Succinic acid forms colourless crystals, which melt at  $180^\circ$ ; at about  $235^\circ$  the acid boils, and is decomposed into succinic anhydride and water. Succinic acid, like the previous acid (oxalic), forms two classes of salts, its compounds with the alkali metals being soluble. Ferric succinate is brown and insoluble. Succinic acid forms substitution products with chlorine and bromine. An isomeric modification of succinic acid, called iso-succinic acid, is known.

PYROTARTARIC ACID. (*See tartaric acid.*)

SUBERIC ACID is a product of the oxidation of cork by nitric acid.

SEBACIC ACID is formed during the destructive distillation of oleic acid.

MALIC SERIES OF DIBASIC ACIDS—

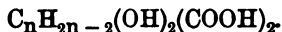


The chief member of this series is *Malic Acid*.

MALIC ACID,  $C_4H_6O_5 = C_2H_3(OH)(COOH)_2$ , is very widely diffused throughout the vegetable kingdom, being

met with both in the free state and as salts of potassium, magnesium, and calcium. Malic acid is a constituent of the juice of most fruits, being specially abundant in the berries of the mountain ash, and in the ordinary garden rhubarb. It can be produced by the action of argentic oxide and water on mono-bromo-succinic acid. Malic acid, by exposure to a temperature of  $180^{\circ}$ , loses a molecule of water, and yields a different acid, having the formula,  $C_4H_4O_4$ . Heated with hydriodic acid malic acid is converted into succinic acid.

#### TARTARIC SERIES OF DIBASIC ACIDS—



Of this series the most important member is *Tartaric Acid*.

TARTARIC ACID ( $C_4H_6O_6 = C_2H_2(OH)_2(COOH)_2$ ) occurs to a large extent in the vegetable kingdom, being generally associated with oxalic, malic, and citric acids. Tartaric acid is generally prepared from an impure acid potassium tartrate, called *argol* or *tartar*, which is deposited during the fermentation of grape juice in the manufacture of wine. The tartaric acid of the *argol* is converted into an insoluble lime salt, which is then decomposed by sulphuric acid, insoluble calcium sulphate and free tartaric acid being formed. Tartaric acid may be also produced by the action of nitric acid on milk sugar. This acid is singular in yielding several modifications, as shown in the following table:—

NAME	CHARACTERISTICS
Dextrotartaric acid . . . . . (The ordinary acid)	{ Turns the plane of polarisation to the right.
Lævotartaric acid . . . . .	
Racemic or paratartaric acid	{ Turns the plane of polarisation to the left.
Inactive or mesotartaric acid	{ Neutral on polarised light, but may be resolved into dextro and lævo-tartaric acids.
Metatartaric acid . . . . .	{ Also optically inactive, but cannot be resolved into dextro and lævo-modifications.
	Uncrystallisable.

Ordinary tartaric acid crystallises in large prisms, which dissolve freely in water. By fusion it is converted into metatartaric acid, and at a temperature of  $180^{\circ}$  it undergoes decomposition, evolving a peculiar odour. By the action of oxidising agents it is converted into formic and oxalic acids, and carbon dioxide, and by fusion with caustic potash acetic and oxalic acids are produced. By dry distillation it yields pyrotartaric acid. Tartaric acid is carbonised by strong sulphuric acid. Heated with hydriodic acid, it loses first one atom of oxygen, and yields malic acid, and then a second atom of oxygen, and becomes succinic acid. Like oxalic, tartaric acid forms two classes of salts, the normal potassium compound,  $K_2C_4H_4O_6$ , being freely soluble in water, while the acid compound, hydrogen potassium tartrate,  $KHC_4H_4O_6$ , is very slightly soluble. The compound which tartaric acid forms with antimony (tartar emetic) has been already described.

**FUMARIC SERIES OF DIBASIC ACIDS** ( $C_nH_{2n-2}(COOH)_2$ )  
Of this series the two following compounds may be mentioned :—

**FUMARIC ACID**,  $C_4H_4O_4$ , and its isomeric modification, *malleic acid*, are produced by heating malic acid to  $180^{\circ}$ , when it loses a molecule of water,  $C_4H_6O_5 = C_4H_4O_4 + H_2O$ . Both these acids unite directly with hydrogen to form succinic acid.

### TRIBASIC ACIDS

Of these acids one only need be mentioned, viz., *Citric acid*, belonging to the  $C_nH_{2n-1}(COOH)_3$  group.

**CITRIC ACID**,  $C_6H_8O_7 = C_3H_4(OH)(COOH)_3$ , occurs in association with tartaric, malic, and oxalic acids, and is especially abundant in the juice of such fruits as the lemon and lime. It forms large colourless crystals, which are freely soluble in water. When heated it loses water and becomes aconitic acid, which occurs in

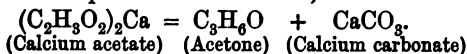
the monkshood. It is decomposed by concentrated sulphuric acid. Being tribasic, citric acid forms three series of salts, in which one, two, or the whole of the replaceable hydrogen is displaced by a base. The citrates of the alkali metals are soluble, those of the alkaline earth metals are insoluble.

Some further acids may be mentioned not belonging to any of the previous series, viz., *phthalic acid* and *isophthalic acid*, isomeric with *terephthalic acid*,  $C_6H_4(COOH)_2$ , which are products of the oxidation of turpentine and other hydrocarbons by nitric acid. *Mellitic acid*,  $C_6(COOH)_6$ , occurs in *mellite* or *honey-stone* as an aluminate. Mellite occurs in large crystals in the brown coal formation.

### KETONES

The ketones are a class of bodies produced by the oxidation of the secondary alcohols in the same way that the aldehydes are formed from the oxidation of the primary alcohols. They may be regarded as aldehydes in which the H of the group COH has been replaced by a monad hydrocarbon radical. The aldehydes yield by oxidation acids containing the same number of carbon atoms as the corresponding hydrocarbon. Ketones, on the contrary, yield acids containing a smaller number of carbon atoms. Thus, normal primary ethyl alcohol,  $C_2H_5O$ , yields on oxidation acetic aldehyde,  $C_2H_4O$ , and then acetic acid,  $C_2H_4O_2$ , the alcohol and its oxidation products containing the same number of carbon atoms. The normal secondary alcohol, dimethyl carbinol,  $C_3H_8O$ , yields on oxidation a ketone (acetone),  $C_3H_6O$ , and on further oxidation, acetic acid,  $C_2H_4O_2$ , and carbonic acid,  $CO_2$ , the produced acids each containing a less number of carbon atoms than the original alcohol. Many ketones are known, but the most important one, and that which has received the most attention, is ordinary acetone.

Acetone,  $\left. \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} \right\} \text{CO}$ , *dimethyl ketone*, is best obtained by the decomposition of an acetate, thus—



Acetone is a limpid inflammable liquid of specific gravity 0.79, and boiling at 56°. It has an agreeable odour. It dissolves in water in all proportions. When acted on by potassium dichromate and sulphuric acid it is decomposed into acetic and carbonic acids.



By the action of nascent hydrogen, evolved by sodium amalgam and water, acetone takes up hydrogen and becomes the normal secondary alcohol, dimethyl carbinol,  $\text{C}_3\text{H}_6\text{O} + \text{H}_2 = \text{C}_3\text{H}_8\text{O}$ .

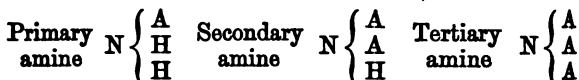
#### THE AMINES OR ORGANIC AMMONIAS

The amines are all regarded as built on the ammonia

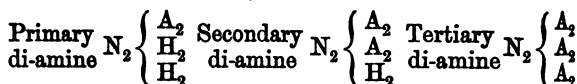
type,  $\text{N} \begin{Bmatrix} \text{H} \\ \text{H} \\ \text{H} \end{Bmatrix}$ , and may be regarded as ammonia in

which a part, or the whole, of the hydrogen is replaced by hydrocarbon groups. From these hydrocarbon groups generally being alcohol radicals, the amines are sometimes called the *compound alcoholic ammonias*. This substitution may take place in one, two, or three molecules of ammonia, giving rise to mon-amines, di-amines, and tri-amines. In these compounds the nitrogen may be replaced by phosphorus, arsenic, or antimony, giving rise to compounds which are termed respectively phosphines, arsines, and stibines, which are bases analogous in composition and properties to the amines. A large number of the natural vegetable alkaloids are regarded as tertiary amines, but they will be considered in a distinct chapter. The mon-amines, di-amines, and tri-amines are divided into primary, secondary, and tertiary, according to the number of the

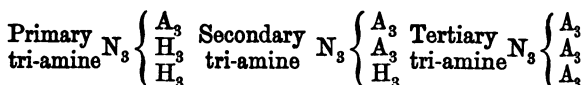
hydrogen atoms in the ammonia molecule, which are replaced by an organic radical, thus—let “A” represent the organic monad radical, and we have the following mon-amines :—



In the di-amines, which are formulated on the model of two molecules of ammonia, “A” representing the monad radical as before, we have—

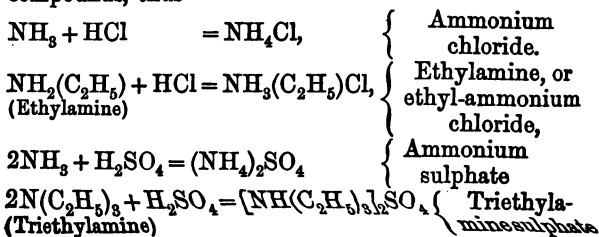


In the same way the tri-amines are formulated on three molecules of ammonia—



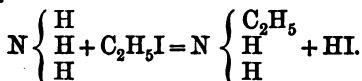
In the secondary and tertiary amines the hydrogen may be replaced, not only by groups of the same radical, but by those of a different radical, so that a secondary amine may contain ethyl and methyl radicals, and a tertiary amine, ethyl, methyl, and amyl.

The amines are, as a rule, a class of bodies possessing basic properties, and uniting with acids to form well-defined salts, analogous to the corresponding ammonium compounds, thus—



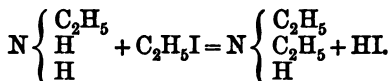
Besides these simple salts, the amines form double salts with platinic chloride, the compounds so produced being peculiar in increasing in solubility in proportion to the number of organic radicals contained in the amine. The amine sulphates also unite with aluminium sulphate to form alums which are isomorphous with ordinary alum.

The most important amines are those containing the radicals methyl, ethyl, amyl, and phenyl. The amines may be produced in many ways, among others by the action of caustic alkalis on the cyanates of alcohol radicals, and by the action of the haloid derivatives of the hydrocarbons on ammonia, by which a haloid salt of the organic ammonia is formed, which is subsequently decomposed by potash. The following shows the action:—

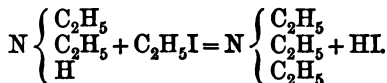


Ammonia + Ethyl iodide = Ethylamine + Hydriodic acid.

By acting on the ethylamine (primary amine) with ethyl iodide a second group of  $\text{C}_2\text{H}_5$  is substituted for hydrogen, and the secondary amine, di-ethylamine, is produced thus—



While, by the further action of ethyl iodide, the tertiary amine, tri-ethylamine, is formed—



These ethylamines resemble the corresponding methyl compounds. When tri-ethylamine is subjected to the action of ethyl-iodide, a compound called tetrethyl-ammonium iodide is formed, which is converted in



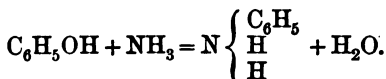
part by the action of caustic potash into *tetrethyl-ammonium hydrate*,  $N(C_2H_5)_4OH$ , a substance closely resembling caustic potash in its properties, being soluble in water, powerfully caustic, and precipitating metallic oxides from their solutions.

**METHYLAMINE**,  $CH_3NH_2$ , is a gaseous body, closely resembling ammonia in its properties, having a strong ammoniacal odour, a powerful alkaline reaction, and being very soluble in water. It is, however, distinguished from ammonia in being inflammable, burning with a yellow flame; it may be formed by the action of nascent hydrogen on prussic or on formic acid.

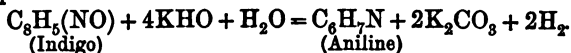
**DIMETHYLAMINE**,  $(CH_3)_2NH$ , resembles the previous compound, and liquefies at  $8^\circ$ .

**TRIMETHYLAMINE**,  $(CH_3)_3N$ , is metameric with methyl-ethylamine and propylamine. It occurs in many animal fluids, notably in herring brine, and possesses a fish-like ammoniacal odour, and boils at  $9.3^\circ$ .

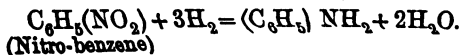
**PHENYLAMINE**,  $(C_6H_5)NH_2$ , better known as aniline. This compound may be regarded as the amine of phenyl, or as amidobenzene, that is, benzene,  $C_6H_6$ , in which one atom of hydrogen is replaced by the monad group ( $NH_2$ ). Aniline may be formed by heating phenol with ammonia in a tube for two or three weeks—



It may also be obtained by heating indigo with caustic potash—



It is, however, generally formed by reducing nitrobenzene by means of the nascent hydrogen evolved by the action of acetic acid on iron filings—



Aniline is a colourless liquid of peculiar odour. It boils at  $182^{\circ}$ , and has a specific gravity of 1.036 at  $0^{\circ}$ . It is soluble in alcohol and ether, but is nearly insoluble in water. It does not turn reddened litmus paper blue, but forms definite salts with acids. Aniline occurs in small quantity in coal tar. It has of late assumed great importance, in being used for the preparation of the so-called aniline colours. In practice, it is formed from the benzol obtained from the distillation of the lighter portions of coal tar, the benzol being converted into nitro-benzol, and this into aniline. Aniline may be recognised in very small quantity by adding an alkaline hypochlorite to an aqueous solution of any of its salts, when a splendid violet coloration is produced, which, however, fades very quickly. This colour is one of the most important aniline dyes, viz., *mauve*. Aniline gives numerous derivatives formed by the replacement of the two hydrogen atoms of the amine by hydro-carbon radicals.

### ANILINE COLOURS

*Mauve*.—The commercial colour of this name is the sulphate of a base called *mauveine*,  $C_{27}H_{24}N_4$ . The best ways of preparing mauve are (1.) by adding dilute solution of potassium dichromate to a solution of aniline sulphate, also dilute; (2.) by heating aniline with a double chloride of sodium and copper. Mauve is a brittle substance, having a beautiful bronze-coloured surface. It is very slightly soluble in cold water, but soluble in alcohol and concentrated acetic acid.

*Aniline red*.—Rosaniline occurs in commerce as roseine, fuchsin, magenta, etc. These compounds are monacid salts of the base rosaniline,  $C_{20}H_{19}N_3$ , the acetate being the chief salt met with. The commercial colour is produced by heating a mixture of aniline and arsenic acid. Rosaniline is peculiar in being colourless in the *free state*, while its acid compounds have an intense red

colour. The base is insoluble in water, while its salts are soluble.

*Aniline blue and aniline violet* may be produced by heating rosaniline with an excess of aniline. The blue compound is a hydro-chloride of triphenyl—rosaniline,  $C_{30}H_{16}(C_6H_5)_3N_3$ . If the three molecules of phenyl,  $C_6H_5$ , in this compound are replaced by methyl or ethyl, a colour known as Hofmann's violet,  $C_{20}H_{16}(C_2H_5)_3N_3$  is formed.

*Aniline yellow* is an isomeric non-explosive modification of diazo-amido-benzene. By acting on aniline nitrate with nitrous acid one atom of nitrogen replaces two atoms of the hydrogen, and diazo-benzene nitrate,  $C_6H_5N_2NO_3$ , is formed, a crystalline compound, exploding by heat or percussion. This combines with aniline to form diazo-amido-benzene. A further yellow, termed *chrysaniline*,  $C_{20}H_{17}N_3$ , is a well-defined base occurring as a secondary product in the preparation of aniline red. A further colouring matter, of a bright yellowish-red tint, called *aurine*, *coralline*, or rosolic acid,  $C_{20}H_{14}O_3$ , is obtained by heating phenol with oxalic and sulphuric acids. In the preparation of the red and violet aniline colours it is found necessary that the aniline used should contain toluidine,  $C_7H_9N$ . This substance is always present in commercial aniline, from the fact that the commercial benzol used for the preparation of nitro-benzol contains toluene, which suffers the same transformations as the benzol, becoming successively nitro-toluene and toluidine.

### THE VEGETABLE ALKALOIDS

These bodies are presumed to bear a close relation to the organic ammonias, but none of them have as yet been artificially prepared. They are found in various plants, and contain as their constituents, carbon, hydrogen, oxygen, and nitrogen. The majority of the vegetable alkaloids are solid, but some few are liquid.

and volatile, and contain only carbon, hydrogen, and nitrogen as constituents. The alkaloids generally exert a marked influence on polarized light, some rotating the plane of polarisation to the left, and others to the right. Like organic ammonias they form well-defined salts with acids, and crystallisable double compounds with platinic chloride. The vegetable alkaloids are more especially distinguished by numbering among their members some of the most powerful of the known poisons, while others form valuable medicines. The alkaloids may be divided, for the sake of simplicity, into two groups, the members of the first of which contain only carbon, hydrogen, and nitrogen, as ingredients, whilst the members of the second contain oxygen in addition.

#### FIRST GROUP

*Piperidine*,  $C_5H_{10}NH$ , is obtained by distilling piperine,  $C_{17}H_{19}NO_3$ , with an alkali. It is a colourless liquid, boiling at  $106^\circ$ , possessing a mingled odour of pepper and ammonia. One of its hydrogen atoms can be replaced by an organic alcohol radical. *Conine*,  $C_8H_{14}NH$ , occurs in "*conium maculatum*," the common hemlock. It is a volatile, oily liquid, possessing a strong alkaline reaction, and forming crystallisable salts with acids. It is a powerful narcotic poison.

*Nicotine*,  $C_{10}H_{14}N_2$ , is found in tobacco, which contains from two to eight per cent. of the alkaloid. It is an oily liquid, boiling at about  $240^\circ$ , at the same time undergoing a certain amount of decomposition. It is soluble in water, alcohol, and ether, and is one of the most powerful of known poisons.

#### SECOND GROUP

*Alkaloids of Opium.* Opium, which is the inspissated juice of the capsule of the white poppy (*Papaver somniferum*), is imported to a large extent from Turkey.

Egypt, and India; that from Turkey being reckoned the best. It consists of gummy, resinous, and colouring matters, together with several alkaloids, of which morphine and narcotine are present in the largest quantity. The following are the opium alkaloids:—

Morphine, $C_{17}H_{19}NO_3$ .	Papaverine, $C_{20}H_{21}NO_4$ .
Codeine, $C_{18}H_{21}NO_3$ .	Narcotine, $C_{22}H_{23}NO_7$ .
Thebaine, $C_{19}H_{21}NO_3$ .	Narceine, $C_{23}H_{29}NO_9$ .

Opium contains in addition a crystalline neutral substance, meconine,  $C_{10}H_{10}O_4$ , and also an acid, meconic acid,  $C_7H_4O_7$ , with which the alkaloids are in combination. In small doses opium forms a most valuable sedative, but in larger quantities it acts as a narcotic poison. Of the opium alkaloids thebaine is the most poisonous.

MORPHINE,  $C_{17}H_{19}NO_3 + H_2O$ , is prepared from opium by treating the aqueous extract with calcium chloride, in order to precipitate the meconic acid, and subsequently evaporating the filtrate, when the morphine separates out as crystalline hydrochloride, from which the alkaloid may be obtained by re-solution and precipitation with ammonia. Morphine is very slightly soluble in cold water, insoluble in ether, but freely soluble in hot alcohol. It forms crystalline salts with acids which are soluble in water. Morphine is distinguished by forming a deep bluish colour with ferric chloride; by heating morphine with hydrochloric acid under pressure it loses  $H_2O$ , and becomes apomorphine,  $C_{17}H_{17}NO_2$ .

CODEINE,  $C_{18}H_{21}NO_3$ , is left in the mother liquors after the crystallisation of morphine; it is soluble in 80 parts of cold and 17 of boiling water. It has a strong alkaline reaction, and forms crystalline salts with acids. Codeine is sometimes called methyl-morphine, and formulated,  $C_{17}H_{18}(CH_3)NO_3$ , from the fact that when treated in a sealed tube with excess of

hydrochloric acid it is converted into apomorphine and methyl-chloride.

THEBAINE,  $C_{19}H_{21}NO_3$ , or paramorphine, exists in very minute quantity in opium, and is but sparingly soluble in water, but dissolves in alcohol and ether. It is the most poisonous of the opium alkaloids.

PAPAVERINE,  $C_{20}H_{21}NO_4$ , is little known, but distinguished from the other opium alkaloids by assuming a deep blue colour on the addition of strong sulphuric acid.

NARCOTINE,  $C_{22}H_{23}NO_7$ , is found in the portion of opium which is insoluble in water, from which it is extracted by boiling with dilute acetic acid. From the solution so obtained the narcotine may be precipitated by the addition of ammonia. It does not possess an alkaline reaction, and although dissolving in acids, does not form crystallisable compounds with them. By heating with caustic potash narcotine yields methy-lamine, di and trimethylamine, and ammonia.

NARCEINE ( $C_{23}H_{29}NO_9$ ), codamine, laudanine, and a few other bases found in very small quantity in opium, are comparatively unimportant.

#### ALKALOIDS OF THE STRYCHNOS

The seeds of the *Strychnos nux vomica*, and the *Strychnos ignatus*, or "St Ignatius bean," contain two exceedingly poisonous alkaloids, known respectively as *strychnine* and *brucine*. *Strychnine*,  $C_{21}H_{22}N_2O_2$ , is a well defined alkaloid, of which the Ignatius bean contains about one and a half per cent., from which it is separated by boiling with dilute sulphuric acid, and crushing, and subsequently treating the expressed liquid with calcium hydrate, which throws down the strychnine and brucine; by treating the precipitate with boiling alcohol the alkaloids are extracted. Strychnine is slightly soluble in water, and acts as a most violent poison. Both the alkaloid and its salts have

an intensely persistent bitter taste. The smallest quantity of solid strychnine may be identified by yielding with sulphuric acid and potassium dichromate an intensely purple coloration, which changes in a short time to red, and finally to yellow.

BRUCINE,  $C_{23}H_{26}N_2O_4 + 4H_2O$ , is found in nuxvomica together with strychnine, and singly in false angustura bark. Brucine is more soluble in water than strychnine, and dissolves readily in alcohol. It forms crystalline compounds with acids, and is less poisonous than strychnine. It may be identified by producing a bright red colour with nitric acid.

#### ALKALOIDS OF THE CHINCHONAS

The valuable medicinal properties of the bark of the Chinchonas, more commonly known as Peruvian bark, are due to the alkaloid quinine which occurs in the bark in conjunction with cinchonine, both alkaloids being in combination with quinic acid.

*Quinine and Cinchonine.*—These alkaloids are prepared by adding a slight excess of calcium hydrate to a strong decoction of Peruvian bark in acidulated water, and boiling the precipitate produced in alcohol: the solution deposits the alkaloids on cooling. They may be separated by conversion into sulphates and crystallisation, the quinine salt separating out first, from being the less soluble of the two. Pure quinine,  $C_{20}H_{24}N_2O_2$ , may be precipitated from the solution of its sulphate by the addition of ammonia as a white crystalline powder. It is soluble in two parts of alcohol, but requires 350 parts of cold water for solution, the aqueous liquid possessing a strong bitter taste. Cinchonine,  $C_{20}H_{24}N_2O$ , is a strong base, and forms salts with acids, which are more soluble both in water and alcohol than those of quinine. Cinchonine does not possess such powerful febrifuge properties as quinine. Quinine and cinchonine may be distin-

guished in solution by the addition of a little chlorine water, followed by an excess of ammonia, when quinine gives a green colour, and cinchonine shows no coloration. A solution of quinine in chlorine water gives a deep red colour with powdered potassium ferrocyanide. Quinine and cinchonine are further distinguished by their action on polarised light, the former giving a powerful left-handed, and the latter a strong right-handed rotation. Besides the two alkaloids named, Peruvian bark contains quinidine, which is isomeric with quinine, and cinchonidine, isomeric with cinchonine. Two further isomeric modifications of the alkaloids are known, viz., quinicine, produced by heating quinine, and cinchonicine, obtained by the action of heat on cinchonine sulphate.

#### VEGETABLE ALKALOIDS FROM OTHER SOURCES

THEOBROMINE,  $C_7H_8N_4O_2$ , is the alkaloid of cocoa theobromo (cacao). It is crystallisable, and not very soluble in water. By the substitution of methyl for one of the constituent hydrogen atoms caffeine is formed.

CAFEINE OR THEINE,  $C_8H_{10}N_4O_2$ , occurs in tea and coffee, and also in the leaves of *Ilex paraguensis*, and *Guarana officinalis*. Theine possesses feebly basic properties, and is soluble in about 100 parts of cold water. Many other alkaloids are known, which, however, being of little importance, need not receive attention here.

#### METALLIC AMINES

These compounds are in reality amines, containing a metal in place of nitrogen. They are frequently termed *phosphines*, *arsines*, and *stibines*, and may be regarded as phosphoretted, arseniuretted, and anti-



monetted hydrogen, in which one or more of the hydrogen atoms is replaced by organic radicals.

Of the phosphorus compounds the following may be taken as examples :—

MONOMETHYL PHOSPHINE,  $P \begin{Bmatrix} CH_3 \\ H \\ H \end{Bmatrix}$  is a colourless gas, in this respect resembling phosphuretted hydrogen,  $P \begin{Bmatrix} H \\ H \\ H \end{Bmatrix}$ . Trimethyl phosphine,  $P \begin{Bmatrix} CH_3 \\ CH_3 \\ CH_3 \end{Bmatrix}$ , resembles the corresponding ethyl compound.

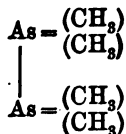
MONO-ETHYL PHOSPHINE,  $P \begin{Bmatrix} C_2H_5 \\ H \\ H \end{Bmatrix}$  and di ethyl phosphine,  $P \begin{Bmatrix} C_2H_5 \\ C_2H_5 \\ H \end{Bmatrix}$ , have been obtained by acting on phosphonium iodide,  $PH_4I$ , with ethyl iodide in presence of zinc oxide at a temperature of  $150^\circ$ . Mono-ethyl phosphine is a colourless volatile liquid, boiling at  $25^\circ$ , possessing a strong unpleasant odour; diethyl phosphine is also a colourless liquid of powerful odour; its boiling point is  $85^\circ$ .

TRIETHYL PHOSPHINE,  $P \begin{Bmatrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{Bmatrix}$ , may be regarded as the most important of the phosphorus bases. It is obtained by the action of phosphorus trichloride on zinc ethyl. It is a colourless oily liquid, boiling at  $133^\circ$ , and possessing a penetrating and disagreeable odour. It is slowly oxidised by exposure to air, and unites with acids to form crystalline deliquescent compounds. Triethyl phosphine unites with sulphur and chlorine, and forms compounds with the iodides of ethyl, methyl, and amyl.

Of the arsenic compounds the most important is—

DI-METHYL ARSINE, or Cacodyl,  $As_2(CH_3)_4$ . This

substance, if regarded as formulated on the type of two molecules of arseniuretted hydrogen, is not a fully saturated compound. It may, however, be regarded as containing trivalent arsenic, of which one of the bonds in each of the atoms are satisfying each other, the two remaining bonds being in union with methyl, thus—



Cacodyl, which derives its name from its offensive odour, is prepared by heating arsenic trioxide with potassium acetate. It is a colourless liquid, boiling at  $170^\circ$ , which immediately takes fire on exposure to air. It is very poisonous, and should be prepared only in the open air. Cacodyl unites with chlorine, oxygen, iodine, and cyanogen. The cyanide is one of the most fearful poisons known. By slow oxidation it forms cacodylic acid,  $\text{As}(\text{CH}_3)_2\text{O}(\text{OH})$ , which is crystalline, soluble, and non-poisonous.

TRIMETHYL ARSINE,  $\text{As} \begin{Bmatrix} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{Bmatrix}$ , is a colourless liquid, prepared by acting on methyl iodide with an alloy of sodium and arsenic.

Of the antimony compounds, the only member which need be mentioned is—

TRIETHYL STIBINE,  $\text{Sb} \begin{Bmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{Bmatrix}$ . It is a colourless liquid, taking fire spontaneously on exposure to air. It boils at  $158^\circ$ , and forms compounds with chlorine, sulphur, and oxygen. An analogous bismuth compound, triethyl bismuthine,  $\text{Bi}(\text{C}_2\text{H}_5)_3$ , is known.

## ORGANO-METALLIC COMPOUNDS

Boron, silicon, and many of the metals unite with hydrocarbon radicals, such as ethyl and methyl, to form a singular and important class of compounds, of which a few of the more important members are here given as examples.

**BORIC ETHIDE**, or **BOR-ETHYL**,  $B.(C_2H_5)_3$ , is a colourless liquid of strongly acid odour, prepared by acting on ethyl borate with zinc ethyl. It boils at  $95^\circ$ , and takes fire on exposure to air.

**SILICIC ETHIDE**,  $Si(C_2H_5)_4$ , is a colourless liquid, boiling at  $150^\circ$ , formed by the action of zinc ethide on silicic chloride. A large number of organic compounds, containing silicon, have been prepared bearing a singular analogy to the corresponding carbon compounds, thus—

Silicic hydride,	$SiH_4$ ,	corresponding to	Methane, $CH_4$ .
Silicon chloroform,	$SiHCl_3$ ,	"	Chloroform, $CHCl_3$ .
Silicic chloride,	$SiCl_4$ ,	"	Carbonic chloride, $CCl_4$ .
Silico pentane,	$Si(CH_3)_4$ ,	"	Pentane, $C(CH_3)_4$ .
Silico-formic acid,	$HSiO(OH)$ ,	"	Formic acid, $HCO(OH)$ .

**ZINC ETHIDE**, or **ZINC ETHYL**,  $Zn \left\{ \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix} \right.$ , is an important compound produced by the action of metallic zinc upon ethyl iodide. It is a mobile, colourless, spontaneously inflammable liquid, which boils at  $118^\circ$ . It is decomposed by water with formation of ethane and zinc hydrate. By slow oxidation, zinc ethyl may be converted into zinc ethylethylate,  $Zn \left\{ \begin{smallmatrix} C_2H_5 \\ OC_2H_5 \end{smallmatrix} \right.$ , and eventually into zinc ethylate,  $Zn \left\{ \begin{smallmatrix} OC_2H_5 \\ OC_2H_5 \end{smallmatrix} \right.$ . By the action of zinc ethyl on silicon tetrachloride, silicon ethide is formed, while, by its action on metallic chlorides, the corresponding metallic ethides are formed. The mercury compound,  $Hg(C_2H_5)_2$ , is very poisonous.

## ANIMAL CHEMISTRY

THIS branch of chemistry is one which presents the greatest difficulties to the investigator, partly for the reason that many of the substances which exist in great quantity, and are of the greatest importance in the animal economy, are non-crystalline, and cannot therefore be obtained in a state of absolute purity; and partly from the fact that the chemical methods employed to isolate these substances, frequently effect such changes in them that it is often exceedingly doubtful whether the compounds ultimately obtained do or do not form a part of the animal body. A special class of compounds which form the basis of the animal structure are the so-called *albuminoids* or *proteids*. These bodies form the principal solid constituents of blood, muscles, nerves, glands, and the organs of animals generally, and many of them are also present in vegetables. The molecular weight and actual constitution of these compounds is not known, but their percentage composition has been determined, and is as follows:—

Carbon,	52·7 to 54·5
Hydrogen,	6·9 to 7·3
Nitrogen,	15·4 to 16·5
Oxygen,	20·9 to 23·5
Sulphur,	0·8 to 1·6

It will be seen from the above numbers that the variation in the percentage compositions of the elements which go to form albuminous compounds is very slight.

and that one of the most characteristic features of their composition is the large amount of nitrogen present. The albuminoids are amorphous, gelatinous bodies, more or less insoluble in water, soluble in excess of acetic acid, and freely dissolved by alkalis; they are almost insoluble in alcohol, and absolutely insoluble in ether. Strong hydrochloric acid acts on them with production of *syntonin* or *acid albumin*, which is soluble in water, and is not coagulated by heat, and the solutions of which, when neutralised by an alkali, yield insoluble albumen as a precipitate. Hot solutions of strong caustic alkalis decompose the albuminoids, the products of decomposition varying with the temperature; the chief substances formed are *leucine*, *tyrosine*, *oxalic* and *carbonic acids*, and *ammonia*. The following description embraces the chief albuminoid compounds:—

**ALBUMIN.**—This substance is present in the solid and liquid portions of the animal body. It occurs in the liquid portion of blood, and in the white of egg. It is best prepared from white of egg, either by spreading it over plates of glass to dry, or in a purer condition by briskly agitating the liquid while diluting with water, filtering to remove animal membrane, neutralising the liquid, which is slightly alkaline, with acetic acid, and finally evaporating at a temperature not exceeding 65°. As thus prepared albumin is an amorphous, yellowish, transparent mass, soluble in cold water. When a solution containing albumin is heated to a higher temperature than 65°, it becomes white and opaque, from the separation of the albumin in an insoluble form. This power of coagulation is one of the most characteristic properties of albumin. The coagulation is also affected by strong mineral acids, and precipitation is caused by solutions of many metallic salts, such as mercuric chloride and lead acetate. A distinction is sometimes made between the albumin of egg and that from blood, the latter being called *serum albumin*.

and the former egg albumin. Both varieties coagulate by heat. The insoluble form of substance thus separated from its solutions dissolves freely in solutions of alkalis, forming an alkaline albuminate. The potassium compound may be formed by agitating the white of egg, and then adding potash solution, when a yellow transparent viscid mass is obtained, soluble in water, and not coagulated by heat. From the solution acids precipitate insoluble albumin. A form of albumin exists in vegetables.

GLOBULIN exists in the blood, and is the albuminous constituent of the crystalline lens. It may be prepared from blood serum by diluting with water, and passing a stream of carbonic acid through the solution.

FIBRIN is a peculiar substance, which speedily separates from freshly-drawn blood, in which, however, it does not pre-exist. Fibrin is generally obtained by stirring freshly drawn blood with a bundle of twigs, on which the fibrin is deposited as a greyish-white stringy, extensible solid, which is tasteless, and insoluble in water. Fibrin appears to be produced in the blood after its extraction from the body by the action of a peculiar ferment—the fibrin ferment—on two albuminous substances called fibrinogen, and fibrinoplastic substance. The ferment causes the union of these two materials to form fibrin. When blood is allowed to stand without agitation, it soon begins to assume a gelatinous appearance, and finally separates into a red solid portion or clot (which is a mixture of solidified fibrin and blood corpuscles), and a clear yellow liquid called *serum* or *liquor sanguinis*.

MYROSIN is another albuminous substance which is present in the juice of muscle, but coagulates at death.

GLUTIN is not a constituent of the animal body, but is an albuminoid existing in vegetables. It may be prepared from wheat flour by kneading it in a muslin bag in a stream of water to separate the starch.

Prepared in this manner, however, it contains cellulose and other impurities. It forms a white sticky semi-elastic substance, which may be drawn out into threads. Glutin is a mixture of several albuminous substances, the chief of which is *gliadin*, or vegetable fibrin.

**CASEIN** is the albuminous substance of milk from which cheese is produced. It is an alkaline albuminate. The casein existing in solution in milk is not coagulable by simple boiling, but only by the addition of an acid or of *rennet*, the inner coating of the stomach of the calf; by either addition the casein and butter fat separate as *curds*, the liquid remaining being termed whey, and containing milk sugar and mineral constituents. Casein is also found in vegetables.

**GELATIN** is a substance closely allied to the albuminoids. It is obtained from certain portions of the animal body, more especially from connective tissue, tendons, ligaments, bones, skin, and horny substances, such as nails, hoofs, etc. It does not pre-exist in these materials, but is formed during the exposure to heat and moisture, in boiling. It is soluble in hot water, but is not coagulated either by heat or by acids. It forms an insoluble compound with mercury, but is not precipitated by lead salts. The gelatin obtained from cartilage is often called *chondrine*. Gelatine ranks high as an article of commerce, the purest variety being known as isinglass, and coarser kinds as glue and size.

Other substances which exist to a lesser extent in the animal body will be noticed in the descriptions of the special parts of the organic structure in which they occur. The various solids and fluids of the animal body are made up of the albuminoids, together with certain other organic and mineral compounds.

**BONE** consists mainly of tribasic calcium phosphate, deposited in an organic basis, which yields gelatine on boiling. The bones of the mammalia resemble each other very closely in chemical composition. The

following shows the percentage composition of the bones of man as compared with that of the ox :—

	Human	Ox
Organic matter,	33·30	30·58
Calcium phosphate, with a little calcium fluoride, }	53·04	60·36
Calcium carbonate,	11·30	6·99
Magnesium phosphate,	1·16	2·07
Soda, with a little sodium chloride, }	1·20	
	<hr/> 100·00	<hr/> 100·00

The teeth have a similar composition, with the exception of containing less organic matter.

FLESH consists of muscular fibre, fibrin, albumin, fat, mineral salts, and water, together with smaller quantities of other constituents. The red colour is due to *hæmoglobin*. When fragments of flesh are subjected to pressure, a liquid, known as "juice of flesh," is obtained, which contains *phosphoric*, *lactic*, and *butyric acids*, and also *kreatine*, *inosite*, and saline matters. This juice is distinctly acid ; a curious fact, inasmuch as the blood possesses a distinctly alkaline reaction. Kreatine may be obtained by first precipitating albumen by heat, and separating it by filtration ; solution of baryta is then added to remove phosphoric acid, and the liquid is again filtered, the filtrate being evaporated to the consistence of a syrup, and set aside to cool. The kreatine then separates in crystals. It is a feeble base, but when boiled with acids it is converted into a powerful base called *kreatinine*. Kreatine, when boiled with alkalis, yields *urea* and *sarcosine*. From the liquid left after the crystallisation of kreatine, *inosite* or *sugar of flesh* may be obtained : a sweet substance having the same composition as grape sugar. The principal saline constituents of flesh are the *phosphates* of potash, magnesia, and lime, with a small



quantity of sodium chloride. Potash is chiefly found in flesh, and soda in the blood. According to Liebig, the acidity of flesh is due to acid potassium phosphate, while the alkalinity of the blood, according to the same authority, is due to sodium phosphate. The electric currents observed in muscles are supposed to be due to the mutual action between the acid flesh and the alkaline blood.

**Blood.**—This liquid may be justly regarded as the most important of the animal fluids, as it is from it that the various organs of the body directly receive their nourishment, and by it effete matters are brought to the lungs for oxidation, and carried to the kidneys etc., for elimination. The blood of the higher vertebrate animals is characterised by its red colour, and by its possessing a temperature above the medium in which the animal moves. The bodily heat is directly connected with the energy and activity of respiration. In man, the normal temperature is  $36.6^{\circ}$  ( $98^{\circ}$  F.), while in birds it is occasionally as high as  $42.8^{\circ}$  ( $109^{\circ}$  F.). The temperature of the blood is independent of that of the atmosphere surrounding the animal, so that the bodily heat in the tropics and in the arctic regions is practically constant. Blood is found to consist, on microscopic examination, of a colourless liquid, in which float small red discs, termed blood corpuscles, which vary in size and shape in different animals. Besides these red corpuscles, blood also contains a smaller quantity of colourless discs, termed white corpuscles. The red blood discs in man are round, and have a diameter of about 0.0075 m.m., while in the frog they are about four times this size, and are elliptical in shape. The blood discs consist of a colourless envelope, containing a red fluid termed *haemoglobin*, a substance of complicated structure, chiefly characterised by containing 0.42 per cent. of iron. *Haemoglobin* may be obtained from the blood in the form of small red crystals, visible under a micro-

scope. When treated with dilute acids, hæmoglobin splits up into *albumin* and *hæmatin*, the latter being a red substance, containing about 7 per cent. of iron. The average specific gravity of healthy human blood is 1·055, and its composition is as follows:—

Water,	79·00	} Serum
Albumin,	7·00	
Fat,	0·06	
Salts,	0·94	} Clot
Fibrin,	0·30	
Corpuscles,	12·70	
<hr/>		
100·00		

The spontaneous separation of blood into *clot* and *serum* soon after its withdrawal from the living body has been already noticed. The serum forms a clear yellowish fluid, which has the following average composition in 100 parts:—

Water,	90
Proteid substances,	8 to 9
Fats, extractives and saline matter,	} 1 to 2

The proteids of serum consist mainly of *serum albumin* and *paraglobin*.

The red corpuscles contain 56·5 per cent. of water, and 43·5 per cent. of solids, of which less than one per cent. are inorganic. The perfectly dry organic matter has been found to contain—

Hæmoglobin,	90·54
Proteids,	8·67
Lecithin,	·54
Cholestrin,	·25

The *lecithin* mentioned in the above analysis is a crystalline substance to which the composition  $C_{44}H_{90}NPO_9$  has been assigned. It occurs throughout the body, and is met with in the brain, nerves, and *semen*, and in yolk of egg. Cholestrin will be noticed

under "Bile." The brain has been found to contain a peculiar substance containing phosphorus, called *proto-gon*, from which a base, termed *Neurine*,  $C_5H_{10}NO$ , has been prepared.

### THE ANIMAL SECRETIONS

**SALIVA** is secreted by the different glands of the mouth, and is a mixture of several fluids. In its healthy condition it is a thick, glairy, and somewhat turbid fluid, having an alkaline reaction. Its specific gravity is 1.002 to 1.006, and it contains about 0.5 per cent. of solid matter, of which 0.2 consists of inorganic salts. The organic substances consist of *mucus*, with small quantities of *globulin* and egg albumin, and, in addition, a small quantity of a peculiar ferment called *ptyalin*, which possesses the property of changing starch into glucose. Saliva is remarkable for containing a small quantity of potassium sulphocyanate. The following analysis of saliva is given by Frerichs :—

Water,	994.10
Solids,	5.90
The solids consist of—	
Ptyalin,	1.41
Fat,	0.07
Epithelium and mucus,	2.13
Salts—consisting of sulphocyanide and chloride of potassium, sodium chloride and phosphate, calcium phosphate and magnesium phos- phate,	2.29
	<hr/> 5.90

The average amount of saliva secreted in the twenty-four hours has been estimated at from one to two pounds.

**SWEAT** is a watery fluid poured out from the skin, and containing from 0.5 to 2 per cent. of solid matter.

Sweat has an acid reaction from the presence of *formic*, *acetic*, *butyric*, and *sudoric acids*; small quantities of fatty matter, salts, and urea are also present. The principal salts are the chlorides of potassium and sodium; small quantities of alkaline and earthy phosphates are also present.

GASTRIC JUICE, the secretion from the inner coat of the stomach, is a clear colourless fluid, of specific gravity 1·001 to 1·010, and containing about ·56 per cent. of solid constituents. The composition of these constituents is as follows:—

Inorganic salts, consisting chiefly of alkaline chlorides, together with small quantities of phosphates	} ·24
Organic substances, of which <i>pepsin</i> is the principal constituent	
	} ·32

Healthy gastric juice possesses an acid reaction from the presence of free hydrochloric acid, the average amount of this substance normally present being about ·2 per cent. The digestive action of gastric juice is due to the presence of the pepsin, which is an albuminous substance capable of effecting the solution of the proteid compounds of the food, and converting them into soluble *peptones*.

BILE, the secretion of the liver, is a viscid liquid, which in man is of a bright golden red colour and alkaline reaction. Its average composition in 1000 parts, according to Frerichs, is as follows:—

Water	859·2	} 1000.
Solids	140·8	

The solids consist of—

Bile salts	91·4
Fats, etc.	9·2
Cholestrin	2·6
Mucus and pigment	29·8
Inorganic salts	7·8

The bile salts mentioned in the above analysis consist of the sodium compounds of two peculiar acids, viz.,

*taurocholic acid*,  $C_{26}H_{45}NSO_7$ , and *glycocholic acid*,  $C_{26}H_{43}NO_6$ . By the action of acids on bile a crystalline substance called *taurine*,  $C_2H_7NSO_3$ , is obtained. The same compound has been prepared artificially by heating ammonium isethionate,  $H_4NC_2H_5SO_4$ , which, by loss of a molecule of water, becomes  $C_2H_7NSO_3$ . Ammonium isethionate is the salt of an acid isomeric with ethyl-sulphuric acid. The bile pigments consist of *bilirubrin*, *biliverdin*, and *cholepyrrhin*; it is these pigments which give rise to the characteristic coloration which takes place when bile is treated with nitric acid. The principal pigment of fresh human bile is bilirubrin,  $C_{16}H_{18}N_2O$ , and it is also the pigmentary matter of gall stones. It occurs largely in the urine during jaundice. Bilirubrin exposed to the air in alkaline solution becomes converted into *biliverdin*,  $C_{16}H_{20}N_2O_5$ , which is the green pigment occurring normally in the bile of the herbivora.

**MILK.**—This secretion contains all the materials which are necessary for the sustenance and growth of young animals, but varies considerably in the amounts of its different constituents. Milk consists of a colourless fluid, holding white fat globules in suspension, a large proportion of which rise to the surface of the milk on standing, forming *cream*. By violent mechanical agitation, as in churning, the albuminous envelope of these globules may be ruptured, and the fat liberated. The fluid portion of milk contains milk sugar, casein, and alkaline chlorides and phosphates. The following table gives the average composition of the milk of different animals :—

	Woman	Cow	Ass	Ewe	Mare
Water . .	88.90	87.02	91.65	86.52	89.33
Sugar . .	4.36	4.77	6.08	5.00	8.75
Casein . .	3.92	4.48	1.82	4.50	1.62
Butter . .	2.66	3.13	0.11	4.20	0.20
Salts . .	1.38	0.60	0.34	0.68	

The specific gravity of milk varies from 1.020 to 1.045.

**URINE.**—This secretion is the vehicle by which the waste nitrogenous constituents of the food and of the body are carried away in the form of urea and uric acid. It also provides an exit for superfluous water, and soluble salts. In its normal condition the urine is a light amber-coloured, transparent fluid, of decidedly acid reaction, and specific gravity of from 1·020 to 1·025. It contains in solution urea, uric and hippuric acids, creatine, creatinine, and various salts, such as the sulphates, chlorides, and phosphates of calcium and magnesium. The following shows the per centage composition of normal human urine :—

Water . . . . .	93·30
Urea . . . . .	3·01
Uric acid . . . . .	0·10
Lactates and extractive matter . . . . .	1·71
Mucus of bladder . . . . .	0·03
Phosphates, chlorides, and sulphates . . . . .	1·84
	<hr/>
	99·99

Diseased urine frequently contains other constituents, one of the commonest of which is albumin, which may be detected by acidifying with nitric acid, and boiling, when a white flocculent precipitate is formed. Another abnormal constituent of urine is grape sugar, which, when present in large quantities, constitutes the disease known as *diabetes mellitus*. In this disease the amount of sugar secreted in the urine is frequently sufficient to raise the specific gravity of the liquid to 1·04 and even higher. The presence of sugar may be proved by the test mentioned under *glucose*. In cases where salts of organic acids are being administered as medicine, the urine voided is frequently alkaline from the oxidation of the organic acid in the system, and the consequent production of alkaline carbonate. The urine of the carnivora is acid, and is characterised by containing a large quantity of urea, and small amount of uric acid.

while that of the herbivora is alkaline, and contains hippuric acid, but no uric acid.

The various constituents of urine have been already described, with the exception of *uric acid*. This substance, formerly called *lithic acid*, is essentially a product of the animal organism, and has not, as yet, been prepared by artificial means. It may be prepared from human urine by concentration and addition of hydrochloric acid, but is more easily obtained from the excrement of serpents, which consists almost entirely of uric acid and ammonium urate. In the pure state uric acid is a glistening snow-white powder, which is very sparingly soluble in water, but dissolves in the fixed alkalis to form urates, from which the uric acid is precipitated on the addition of an acid. Uric acid has the composition  $C_5N_4H_4O_3$ ; it is dibasic, the acid salts being sparingly soluble in water. It may be detected even in small quantity by its reaction with nitric acid and ammonia. If a small quantity of uric acid be treated with nitric acid it dissolves with effervescence, and on evaporating the solution to dryness at a gentle heat, and then adding a little water and a drop of strong ammonia, a deep red coloration is produced, due to the formation of murexide.

**URINARY DEPOSITS, CALCULI.**—The examination of urinary deposits often affords a clue to the diagnosis of disease, and is therefore of the greatest importance. The microscope affords valuable assistance in the detection of epithelial cells, etc., and in the identification of such substances as uric acid, phosphate of soda and ammonia, by the form of the crystals. Urinary deposits are of various colours, and the ordinary kinds consist chiefly of phosphates, or acid urates. Deposits of acid urates are generally accompanied by an abnormally acid condition of the urine. They are pink, red, or buff coloured, and are not soluble in dilute hydrochloric acid, but dissolve easily in caustic soda solution. A deposit of earthy phosphates, on the other hand, is

light in colour, and easily dissolved by dilute acids. Urinary calculi are of several kinds, the commonest being the uric acid calculus, the ammonium urate calculus, the fusible calculus, consisting of calcium phosphate and ammonia-magnesian phosphate, and the mulberry calculus, consisting of calcium oxalate. The following method of examination may be used to distinguish the varieties of calculi mentioned.

A little of the finely powdered calculus is boiled with dilute hydrochloric acid—

Insoluble—	Soluble—
Uric acid,	Phosphatic calculus,
Ammonium urate.	Calcium oxalate.

The insoluble powder is heated with solution of caustic soda; if a smell of ammonia is evolved, the calculus is probably ammonium urate; if no odour of ammonia is perceived, uric acid alone is present. In either case confirm presence of uric acid by murexide test. If the calculus has dissolved, take a fresh portion of the finely powdered material and heat in a platinum crucible—

*Phosphatic calculus*

Remains unchanged at a moderate heat, fuses at a higher temperature, the cooled material does not effervesce on addition of dilute HCl.

*Calcium oxalate*

Powder gives a bluish flame, which disappears, leaving a white powder of calcium carbonate, which, when cold, effervesces on the addition of dilute HCl.

## RESPIRATION AND NUTRITION

By these two functions the animal body is maintained in its integrity, the one maintaining animal heat, the other repairing waste of tissue.



**RESPIRATION.**—In the act of respiration the lungs are filled with air, and there the contained blood is aerated, and loses by oxidation various used-up materials, which are, by this means, removed. In all warm-blooded animals there exists two kinds of blood, viz., the arterial, found on the left side of the heart and in arteries, and the venous, occurring on the right side of the heart and in the veins. Venous blood is of a purple hue, and is the blood which, by circulation through the body, has become charged with effete matters, derived from waste of tissue; it contains very little oxygen, but a considerable quantity of carbonic acid. Arriving at the lungs, where a large surface is exposed to the action of the inhaled air, it loses the effete products with which it is charged, together with some carbonic acid, and absorbs a considerable quantity of oxygen, and assumes the bright red colour peculiar to arterial blood. The absorption of oxygen takes place through the agency of the hæmoglobin, with which it forms a very weak compound. The amount of air taken into the lungs in an ordinary inspiration, amounts to from 350 to 700 cubic centimetres. The expired air will not support the combustion of a candle, containing, as it does, from 4 to 5 per cent. less oxygen, and about 4 per cent. more carbonic acid than the inspired air, the amount of nitrogen present suffering but little change. It is also loaded with aqueous vapour, and contains various undetermined organic impurities, which render it far more deleterious to animal life than may be fairly assumed to be due to the increase of carbonic acid. The amount of carbonic acid expired is subject to considerable variations, bodily activity and various other agencies affecting it. It is generally largest in quantity when the respiration is slow, and least when respiration is fast. The carbonic acid of venous blood is supposed to be retained in the form of bicarbonate of soda.

**NUTRITION.**—The various substances used by animals

as food are distinguished by being *organised structures*, plants alone having the power of appropriating *inorganic materials* as food. The first process to which food is subjected is *mastication*, by which it is more or less finely divided. At the same time the food becomes intimately mixed with the saliva, the *ptyalin* of which converts a portion of the starchy substances into sugar. Passing to the stomach it is exposed to the action of the gastric juice, by which the albuminous materials present, such as casein and albumen, are converted into soluble peptones. The gastric juice has no action on sugar or on *fats*, but it prepares the way for the assimilation of the latter by dissolving the gelatiniferous and proteid envelopes in which the fat globules are enclosed. Passing to the small intestine, the partially digested food, or *chyme*, as it is termed, is mixed with the bile, the functions of which appear to be the neutralisation of the acidity of the gastric juice, and the partial emulsion of *fats*. Bile also appears to facilitate the absorption of the nutritive elements from the food, by reason of a peculiar action which it exercises on animal membranes generally. A membrane moistened with bile, or with a solution of a bile salt, offers comparatively little resistance to the passage of *fats*. Even filter paper moistened with bile salts will allow oil to pass through with considerable ease, whereas if the paper is simply moistened with distilled water, the oil will scarcely pass through. The next addition to the partially digested food in its passage through the body, is the pancreatic fluid, a viscid liquid, having an alkaline reaction from the presence of a comparatively large quantity of sodium carbonate. The pancreatic juice acts with great energy on starchy materials, and rapidly converts them into grape sugar; it also converts unaltered proteids into soluble peptones by the action of a peculiar ferment called *trypsin*, which resembles the pepsin of gastric juice. The pancreatic juice has also a distinct action

on fats, emulsifying them, and, at the same time, splitting up the neutral varieties into fatty acids and glycerine, the fatty acids being subsequently, in great measure, converted into soaps. The final action of all the digestive fluids is to convert the greater part of the various constituents of the food, either into a soluble form, or to reduce them to such a fine state of division that they are capable of being absorbed by the blood, and utilised for nutritive purposes. The albuminous substances are supposed to be specially utilised in the formation of flesh and the repair of wasted tissue, while sugars, starches, and fats have the important function of maintaining animal heat. A classification of the various food constituents may be thus made into *flesh formers*, consisting of the proteids, and *heat producers* or carbohydrates. Where the amount of food supplied to the body is insufficient for efficient nutrition, or where food is altogether withheld, as in cases of starvation, the amount of carbonic acid given off from the lungs decreases, and, at the same time, the quantity of urea secreted diminishes. In the case of a dog it was found that with a full diet of flesh and fat, the quantity of carbonic acid and urea excreted was, in the case of the former, three times, and of the latter, two-and-twenty times as great as that produced by the animal when kept in a starving condition.

### THE NUTRITION OF PLANTS

This subject constitutes a distinct branch of chemical science, called agricultural chemistry. Plants differ essentially from animals in the substances which they require as food, being capable of assimilating inorganic materials, while animals can only feed on already organised structures. Plants have therefore the special function of producing from inorganic materials organised structures capable of being assimilated by animals. Under the influence of sun light, plants possess the

power of decomposing carbonic acid, oxygen being evolved, and the carbon assimilated in the formation of tissue. In this decomposition of carbonic acid, an amount of energy is expended, which is reproduced in the form of heat when the organic tissues are burnt and carbonic acid reproduced. It is thus that the heat evolved in the combustion of wood and coal is, in reality, a reproduction of the solar energy which was expended in breaking up the carbonic acid from which the original organic tissues were derived. Although the structure of plants is chiefly organic, certain inorganic constituents are always present, which are left as ash when the plant is burned, and the existence of which appears to be necessary to its well-being and growth. In plant growth the carbon is derived mainly from the atmosphere, while nitrogen, hydrogen, and oxygen, are derived partly from the atmosphere, by the agency of the leaves, and partly from the soil, by means of the roots. The supply of mineral constituents, such as potash, soda, and silica, is obtained directly from the soil, through the agency of the roots which have the power of selecting the necessary constituents. Every time that a particular crop is removed from the ground, a certain amount of mineral constituents are also withdrawn, and the soil is then rendered less capable of nourishing a fresh crop of a similar kind. By cultivating a crop of a different character, however, requiring for its growth a different kind of mineral food, the soil can be again successfully utilised, and it is this principle which underlies what is termed in agriculture, the *rotation of crops*. Sometimes, however, the soil is simply broken up and exposed to the air, in which case it is said to "lie fallow;" by this exposure the potash, in combination with silicic acid in the clay of the soil, is rendered soluble, and other changes are effected by which the soil is again replenished with food available for fresh crops. Another mode of restoring the fertility of ground which has been ex-

hausted by cultivation, is by the use of various manures, which restore to the land equivalent quantities of the materials which have been removed from it. Much valuable information has been collected on the subject of plant growth; but to discuss it in a volume such as this would be entirely out of place. We therefore refer the reader to special treatises on this very important and interesting subject.

## DEFINITIONS:

GIVING CONCISE EXPLANATIONS OF SOME OF THE  
PRINCIPAL TERMS USED IN CHEMISTRY

**ACID.**—A compound containing one or more atoms of hydrogen replaceable by a metal to form a salt.

**ALCOHOL.**—An organic compound regarded as derived from a hydrocarbon by the substitution of the monad radical hydroxyl (OH) for hydrogen.

**ALCOHOLATE.**—A crystalline substance containing alcohol in the place of water of crystallisation.

**ALDEHYDE.**—An organic compound derived by oxidation from a primary alcohol, from which it differs in containing two atoms less hydrogen.

**ALKALI.**—A term generally applied to such bases as potash, soda, and ammonia.

**ALLOTROPIC.**—An expression used to denote the fact of a substance occurring in totally different physical forms. Sulphur, phosphorus, carbon, boron, and silicon afford examples of allotropic modifications.

**AMORPHOUS.**—Not possessing any distinct structure or crystalline form.

**AMINE.**—A term used synonymously with "organic ammonia," and applied to a class of compounds generally regarded as derived from ammonia by the substitution of one or more hydrocarbon groups for hydrogen.

**ANHYDRIDE** signifies literally, without water, and is an expression frequently applied to such substances as  $SO_3$ ,  $N_2O_5$ ,  $P_2O_5$ , etc., which by union with water form

acids. The term "anhydride" is also employed in organic chemistry to define a class of substances differing from the organic acids in being minus the elements of water.

**ANHYDROUS.**—Having no water of composition or crystallisation.

**ARTIAD.**—An element whose atomicity is equal to an even number of hydrogen atoms.

**AROMATIC GROUP.**—A class of hydrocarbons, chiefly characterised by containing a group of six carbon atoms in which, out of the twenty-four bonds of union, eighteen are supposed to be saturated by union of carbon with carbon, leaving only six bonds of union open to external saturation.

**ATOM.**—The smallest part of an elementary body which can enter into, or be expelled from, a chemical compound.

**ATOMIC FORMULÆ.**—Formulæ which represent compounds as composed simply of atoms, and by which chemical equations are expressed in the simplest possible manner, atoms alone being shown as taking part in chemical equations in place of molecules.

**ATOMIC WEIGHTS.**—A series of figures representing the relative weights of the atoms of the various elements, taking hydrogen as unity. These figures really represent the weights of the various elements which would occupy, in the state of gas, the same volume as the unit weight of hydrogen at the same temperature and pressure.

**ATOMICITY.**—A term applied to elements and compound radicals to signify their atom replacing power, taking hydrogen as the unit.

**BASE.**—A compound body, which is capable of partly or wholly neutralising an acid to form a salt.

**BASICITY.**—A term used to express the saturating power of acids. (See also MONOBASIC, DIBASIC, etc.)

**COLLOID.**—A substance which will not pass through a membrane when its solution is submitted to dialysis.

**COMBINING WEIGHT.**—This expression is now generally used in connection with the elements as synonymous with atomic weight, and in connection with compounds, as synonymous with molecular weight.

**COMPOUND AMMONIA.** (See AMINE.)

**COMPOUND ETHER.**—An ether whose molecule contains two hydrocarbon groups of different composition.

**COMPOUND RADICAL.**—A term used to designate certain groups of elements, which, although not always capable of isolation, can be transferred in their integrity from one compound to another, and possess definite atomicities.

**CONSTITUTIONAL FORMULÆ.**—Formulæ which, in addition to shewing the composition of a compound, indicate likewise the manner in which its component elements are supposed to be arranged.

**DIALYSIS.**—A system of analysis founded on the fact that some substances, when in the state of aqueous solution, will pass through a membrane of parchment paper floating on the surface of distilled water, while other substances under like conditions will not pass. The former class of substances are termed *crystalloids*, and the latter *colloids*.

**DIAMINE.**—An amine formulated on the type of two molecules of ammonia.

**DIATOMIC.**—Equivalent in combining power to that of two atoms of hydrogen.

**DIBASIC.**—A term applied to acids which contain two atoms of hydrogen, replaceable by metals to form salts.

**DIFFUSION** (of gases).—The property possessed by gases of different densities of spontaneously mixing when placed in communication with each other.

**DIHYDRIC ALCOHOL.**—An organic compound derived from a hydrocarbon by the substitution of two of the hydroxyl groups, OH, for two atoms of hydrogen.

**DIMORPHOUS.**—Possessing two distinct forms, *crystalline* or otherwise.



**DYAD.**—An element or compound radical, capable of replacing two atoms of hydrogen in combination.

**EFFUSION** (of gases).—A term used to signify the passage of gases through minute orifices.

**EMPIRICAL FORMULÆ.**—Formulæ which show only the components of a compound, without reference to their molecular arrangement.

**ETHER.**—An organic compound which is regarded as the anhydride of the corresponding alcohol, and which consists of two hydrocarbon radicals united with one atom of oxygen.

**EQUIVALENT WEIGHT.**—A number representing the smallest proportion of an element which is equal in combining power to one atom of hydrogen.

**GLYPTIC FORMULÆ.**—A system of formulæ mainly used for lecture demonstration, and consisting of coloured balls representing atoms, and pegs representing the theoretical bonds of attachment by which the balls may be connected together, and a representation of the formation of compounds shown.

**GRAPHIC FORMULÆ.**—Formulæ which are the pictorial representation of glyptic formulæ, and in which the elementary atoms are represented by circles, in which is written the corresponding symbol, while the atomicity and method of attachment is shown by short lines uniting the circles to each other.

**HALOGEN.**—Signifies literally "*salt producer*," but is now applied solely to the elements Chlorine, Bromine, Iodine, and Fluorine.

**HALOID.**—Appertaining to the Halogens.

**HOMOLOGOUS.**—An expression used in Organic Chemistry in connection with certain series of compounds, each member of which differs from the preceding member by an addition of  $\text{CH}_2$ .

**HYDRACID.**—A term generally applied to such acids as  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , and  $\text{HF}$ , consisting of hydrogen united to a haloid element, and having no oxygen in their composition.

**ISOLOGOUS.**—An expression used in Organic Chemistry in connection with those series of compounds of which each member differs from the preceding by the addition of  $H_2$ .

**ISOMERIC.**—Is used in Organic Chemistry to denote, in a general sense, the fact of compounds having the same percentage composition but different molecular weights. In the *restricted* sense, the term isomeric applies to those compounds which have the same percentage composition, the same vapour density, which exhibit a similar chemical behaviour when submitted to the action of reagents, but which differ in such physical properties as boiling point and specific gravity.

**ISOMORPHOUS.**—Signifies literally, possessing the same shape, and is used in connection with compounds of different composition which crystallise in the same forms, and are capable of forming mixed crystals.

**KETONE.**—An organic compound derived from the oxidation of a secondary alcohol, in the same way that an aldehyde is produced from the oxidation of a primary alcohol.

**METAMERIC.**—A term applied to those organic compounds which possess the same percentage composition, and the same vapour density, but which differ in physical properties, and behave dissimilarly under the action of reagents.

**MONAD.**—An element, or compound radical, whose combining power is equal to that of one atom of hydrogen.

**MONAMINE.**—An amine formulated on the type of one equivalent of ammonia.

**MONOBASIC.**—A term used to define acids containing one atom of hydrogen, replaceable by a base to form a salt.

**MONOHYDRIC ALCOHOL.**—An organic compound derived from a hydrocarbon by the substitution of the hydroxyl group (OH) for one atom of hydrogen.

**MOLECULAR FORMULÆ.**—Formulae which show *molecules* as taking part in chemical reaction, in

contradistinction to formulæ in which atoms only are shown.

**MOLECULAR WEIGHT.**—The weight of a molecule of an element or compound. The molecular weights of the elements are twice their atomic weights, with the exception of phosphorus and arsenic, whose molecules contain four atoms, and of mercury and a few other volatile metals, whose molecules contain only one atom. The molecular weight of a compound is the aggregate weight of its constituent atoms.

**MOLECULE.**—The smallest part of an element, or compound, which is capable of existence in the free state.

**MONAMINE.**—An amine regarded as derived from one molecule of ammonia by the replacement of a hydrocarbon group, or hydrocarbon groups, for a corresponding number of hydrogen atoms.

**MONATOMIC.**—Having an equal combining power to that possessed by one atom of hydrogen.

**NORMAL SALT.**—A compound formed from an acid by the substitution of a metal for the whole of its replaceable hydrogen.

**OLEFINES.**—A class of hydrocarbons having the general formula  $C_nH_{2n}$ , and of which *Olefiant Gas*, or *Ethylene*,  $C_2H_4$ , is the first member. Each member of the series differs from the preceding member by an addition of  $CH_2$ .

**PARAFFINS.**—A group of hydrocarbons having the general formula  $C_nH_{2n+2}$ , and which are chiefly characterised by their stability under the influence of powerful chemical agents. The starting point of series is Marsh Gas,  $CH_4$ , and each successive member differs from the preceding member by an addition of  $CH_2$ .

**PENTAD.**—An element or compound radical, whose combining power is equivalent to that of five atoms of hydrogen.

**POLYMERIC.**—A term used in organic chemistry to

denote the fact of certain compounds possessing the same percentage composition, but having different vapour densities.

**PRIMARY ALCOHOL.**—A description of alcohol, the chief characteristic of which is that of yielding on oxidation, first an aldehyde, and subsequently an acid, having the same number of carbon atoms as the alcohol.

**PRIMARY AMINE.**—An amine regarded as derived from one, two, or three molecules of ammonia, by the replacement of one-third of the total hydrogen by a corresponding number of hydrocarbon radicals.

**RATIONAL FORMULÆ.**—Synonymous with constitutional formulæ.

**SALT.**—A compound body derived from the mutual action of an acid and a base, or of a metal and a salt radical.

**SALT RADICAL.**—A substance which forms an acid when combined with hydrogen. The term salt radical is synonymous with "*Halogen*."

**SECONDARY ALCOHOL.**—A description of alcohol, chiefly characterised by yielding on oxidation, firstly, a *Ketone*, and finally, one or more acids of the acetic series, each containing a *less* number of carbon atoms than the original alcohol.

**SECONDARY AMINE.**—An amine regarded as derived from one, two, or three molecules of ammonia, by the replacement of two-thirds of the total number of hydrogen atoms by a corresponding number of hydrocarbon radicals.

**TERTIARY ALCOHOL.**—An alcohol chiefly characterised by yielding as the first and final products of oxidation acids of the acetic series, each containing a less number of carbon atoms than the original alcohol.

**TERTIARY AMINE.**—An amine regarded as derived from one, two, or three molecules of ammonia, by the replacement of the whole of the hydrogen atoms by a corresponding number of hydrocarbon radicals.

**TETRATOMIC.**—Equivalent in combining power to four atoms of hydrogen.

**TETRAD.**—An element, or compound radical, whose combining power is equivalent to that of four atoms of hydrogen.

**TRIAD.**—An element, or compound radical, whose combining power is equal to that of three atoms of hydrogen.

**TRIAMINE.**—An amine formulated on the type of three molecules of ammonia.

**TRIATOMIC.**—Possessing a combining power equal to that of three atoms of hydrogen.

**TRIHYDRIC ALCOHOL.**—An organic compound, derived from a hydrocarbon by the substitution of three of the hydroxyl groups, OH, for three atoms of hydrogen.

**VALENCY.**—Synonymous with “Atomicity” and “Quantivalence.”

**VAPOUR DENSITY.**—The weight of a given volume of an element or compound in the gaseous state, compared with the same volume of hydrogen at the same temperature and pressure.

**VAPOUR TENSION.**—A term used to define the elastic force exerted by the vapour of a substance, expressed in millimetres of mercury, and measured at a specified temperature.

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